

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 354 549
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89114720.9

(51) Int. Cl.⁴: G03C 7/38 , //C07D233/54

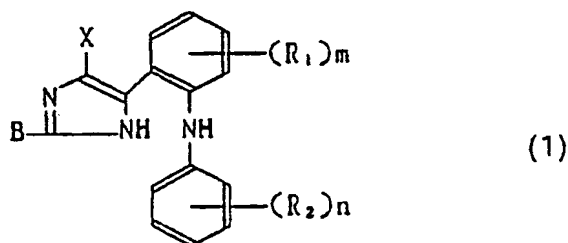
(22) Date of filing: 09.08.89

(30) Priority: 12.08.88 JP 202270/88

(43) Date of publication of application:
14.02.90 Bulletin 90/07(84) Designated Contracting States:
DE GB(71) Applicant: **KONICA CORPORATION**
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku
Tokyo(JP)(72) Inventor: **Masukawa, Toyooki**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Uchida, Takashi**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Nakayama, Noritaka**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)(74) Representative: **Türk, Gille, Hrabal**
Bruckner Strasse 20
D-4000 Düsseldorf 13(DE)

(54) Silver halide photographic lightsensitive material containing novel cyan coupler.

(57) A silver halide color photographic light-sensitive material is disclosed, which has a silver halide emulsion layer containing a novel cyan coupler represented by the following Formula I:



wherein B is an organic group comprising a carbon atom, nitrogen atom, oxygen atom or sulfur atom directly bonded to the imidazole ring; R₁ and R₂ each are a substituent; m is an integer of 0 to 4, n is an integer of 0 to 5, provided that the R₁s or R₂s each may be the same with or different from each other when m or n is 2 or more.; and X is a group capable of being split off upon coupling reaction with the oxidation product of a color developing agent.

EP 0 354 549 A2

SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL CONTAINING NOVEL CYAN COUPLER

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material containing a novel cyan coupler.

BACKGROUND OF THE INVENTION

Phenols or naphthols have been hitherto widely used as cyan couplers used in silver halide photographic light-sensitive materials. These are described, for example, in U.S. Patents No. 2,369,292 and No. 2,474,293.

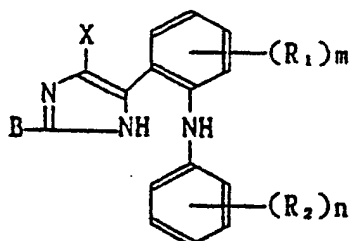
Cyan dye images obtained from the phenols or naphthols, however, have involved great problems in color reproduction. Namely, these cyan color-forming dyes have a poor sharpness at the shortwave side of the absorption spectrum, and also have unwanted absorption at the green portion, as well as at the blue portion in part. In the instances of color photographic papers or color reversal light-sensitive materials, there is no appropriate means for compensating them, making, in the present circumstances, considerably poor the color reproducibility.

The present inventors have now proposed novel cyan couplers, as disclosed in European Patent Application No. 249,453 and Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 226653/1988. In these couplers, the cyan dyes formed have superior spectral absorption characteristics as compared with conventional phenol and naphthol type cyan couplers, bringing about a great improvement in the color reproducibility. They also have a high molar absorptivity of the color-forming dyes, and have made it possible to greatly decrease silver weight as compared with conventional couplers. However, the resulting dye images may have an insufficient fastness, and accordingly it has been sought to newly provide a cyan coupler capable of forming a dye image having a much higher fastness.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a silver halide photographic light-sensitive material that contains a cyan coupler capable of forming a cyan dye having a superior color reproducibility and sufficient fastness, and capable of giving a high color-forming density.

The above object can be achieved by a silver halide photographic light-sensitive material, comprising a support and provided thereon a silver halide emulsion layer containing a cyan coupler represented by the following Formula I.



(I)

wherein B is an organic group comprising a carbon atom, nitrogen atom, oxygen atom or sulfur atom directly bonded to the imidazole ring; R_1 and R_2 each are a substituent; m is an integer of 0 to 4, and n is an integer of 0 to 5, provided that the groups represented by said R_1 and R_2 are respectively allowed to be the same with or different from each other when m or n is 2 or more; and X is a group capable of being

split off upon coupling reaction with the oxidized product of a color developing agent.

DETAILED DESCRIPTION OF THE INVENTION

5

In the above Formula (I), the organic group represented by B, comprising a carbon atom directly bonded to the imidazole ring, includes an alkyl group as exemplified by methyl, i-propyl, t-butyl, trifluoromethyl, benzyl, 3-(4-aminophenyl)propyl, allyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonylethyl, 3-[4-(4-dodecyloxybenzene)sulfonamidophenyl]propyl, 1-methyl-2-[(2-octyloxy-5-t-octylphenyl)sulfonamidophenyl]ethyl, 1-methyl-2-[2-octyloxy-5-(2-octyloxy-5-t-octylphenyl)sulfonamido]phenylsulfonamido]ethyl or 2-[(2-octyloxy-5-(2-octyloxy-5-t-octylphenyl)sulfonamido)phenylsulfonamido]ethyl, an aryl group as exemplified by phenyl, naphthyl, 2,4-dichlorophenyl, 2-hydroxy-5-methylphenyl, 2-acetamidophenyl, 2-methanesulfonamidophenyl, 2-butanamidophenyl, 2-(N,N-dimethylsulfamoylamino)phenyl, 2-(4-dodecyloxybenzenesulfonamido)phenyl, 2-[2-(2,4-di-t-amyloxy)hexanamido]phenyl, 2-(2-octyloxy-5-t-octylphenylsulfonamido)phenyl, 4-carbamoylphenyl, 4-cyanophenyl, 4-carboxyphenyl or 4-ethoxycarbonylphenyl, a heterocyclic group as exemplified by 4-pyridyl or 2-benzimidazolyl; a cyano group, a carboxyl group, an acyl group, a carbamoyl group, an alkoxycarbonyl group, and an aryloxycarbonyl group.

The organic group comprising a nitrogen atom directly bonded to the imidazole ring includes an acylamino group as exemplified by acetamido, benzamido, 2,4-di-t-amyloxyacetamido or 2,4-dichlorobenzamido, an alkoxycarbonylamino group as exemplified by methoxycarbonylamino, propoxycarbonylamino or t-butoxycarbonyl amino, an aryloxycarbonylamino group as exemplified by phenoxycarbonylamino, a sulfonamido group as exemplified by methanesulfonamido, octanesulfonamido, benzenesulfonamido or 4-dodecyloxybenzenesulfonamido, an anilino group as exemplified by phenylamino, 2-chloroanilino or 2-chloro-4-tetradecanamidoanilino, a ureido group as exemplified by N-methylureido, N-butylureido, N-phenylureido or N,N-dibutylureido, a sulfamoylamino group as exemplified by N,N-diethylsulfamoylamino or N-phenylsulfamoylamino, an amino group as exemplified by unsubstituted amino, N-methylamino or N,N-dimethylamino, and a heterocyclic group as exemplified by 3,5-dimethyl-1-pyrazolyl or 2,6-dimethylmorpholino.

The organic group comprising an oxygen atom directly bonded to the imidazole ring includes an alkoxy group as exemplified by methoxy, ethoxy, i-propoxy, butoxy, 2,2,2-trifluoroethoxy, 3,3,3-trifluoropropoxy, 2-chloroethoxy, 2-cyanoethoxy or 2-butanethoxy, an aryloxy group as exemplified by phenoxy, 4-methoxyphenoxy, 2,4-dichlorophenoxy or 4-(2-ethylhexanamido)phenoxy, a silyloxy group as exemplified by trimethylsilyloxy, dimethylphenylsilyloxy or dimethyl-t-butylsilyloxy, and a heterocyclic oxy group as exemplified by tetrahydropyranyloxy, 3-pyridyloxy or 2-(1,3-benzimidazolyl)oxy.

The organic group comprising a sulfur atom directly bonded to the imidazole ring includes an alkylthio group as exemplified by methylthio, ethylthio, butylthio, 3-[4-(4-dodecyloxybenzene)sulfonamidophenyl]propylthio or 4-(2-butoxy-5-t-octylphenylsulfonamido)benzylthio, an arylthio group as exemplified by phenylthio, 2-naphthylthio, 2,5-dichlorophenylthio, 4-dodecylphenylthio or 2-butoxy-5-t-octylphenylthio, a heterocyclic thio group as exemplified by 2-pyridylthio, 2-(1,3-benzoxazolyl)thio, 1-hexadecyl-1,2,3,4-tetrazolyl-5-thio or 1-(3-N-octadecylcarbamoyl)phenyl-1,2,3,4-tetrazolyl-5-thio.

There are no particular limitations on the substituent represented by R₁ and R₂ each, but it may include, for example, a halogen atom, and groups such as cyano, nitro, carboxy, alkyl, alkoxy, carbamoyl, sulfamoyl, acyl, acyloxy, alkoxycarbonyl, alkylamido, arylamido, alkylsulfonamido, arylsulfonamido, dialkylcarbamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, and sulfamoylamino.

Preferred as the alkyl group represented by R₁ and R₂ each is a straight-chain or branched alkyl group having 1 to 22 carbon atoms, including, for example, groups such as methyl, ethyl, butyl, and dodecyl. These alkyl groups also include a cycloalkyl group such as a cyclohexyl group or may be substituted. Preferred substituents include a halogen atom, a hydroxy group, a carboxy group, a cyano group, a sulfo group, and an alkoxy group having 1 to 22 carbon atoms.

Preferred as the alkoxy group is a straight-chain or branched alkoxy group having 1 to 22 carbon atoms, including groups such as methoxy, ethoxy, i-propoxy, octyloxy, and dodecyloxy.

The carbamoyl group includes an unsubstituted alkylcarbamoyl group such as an ethylcarbamoyl or dodecylcarbamoyl group, and a substituted alkylcarbamoyl group such as a diethylcarbamoyl, butyloxypentylcarbamoyl or dodecyloxypropylcarbamoyl group.

The sulfamoyl group also similarly includes an unsubstituted alkylsulfamoyl group such as an ethylsulfamoyl, diethylsulfamoyl or dodecylsulfamoyl group, and a substituted alkylsulfamoyl group such as a

dodecyloxypropylsulfamoyl group.

The arylcarbamoyl group includes a phenylcarbamoyl group and a substituted phenylcarbamoyl group. The arylsulfamoyl group includes a phenylsulfamoyl group and a variety of substituted phenylsulfamoyl groups.

There are also included an acyl group such as an acetyl, benzoyl, butanesulfonyl or benzenesulfonyl group, an acyloxy group such as an acetoxy, lauroyloxy or butanesulfonyloxy group, and an alkoxy-carbonyl group such as an ethoxycarbonyl, i-propyloxycarbonyl or 2-ethylhexyloxycarbonyl group.

The alkylamido group includes a substituted or unsubstituted alkylamido group having 1 to 22 carbon atoms. Typical examples of an unsubstituted alkylamido group includes an acetamido group, a butanamido group, a laurylamido group, and a stearyl-amido group. It may also include an alicyclic amido group such as a cyclohexanecarbonamido group. It may also have a branched structure as exemplified by a 2-ethylhexanamido group or may contain an unsaturated bond.

A substituted alkylamido group of the above alkylamido group includes a halogen-substituted alkylamido group such as a monochloroacetamido, trichloroacetamido or perfluorobutanamido group, and a phenoxy-substituted alkylamido group such as a m-pentadecylphenoxyacetamido, α -(2,4-di-t-amylphenoxy)-pentanamido, α -(2,4-di-t-acylphenoxy)acetamido or o-chlorophenoxy-myristic acid amido group.

The arylamido group also includes a substituted or unsubstituted arylamido group. It typically includes an unsubstituted arylamido group such as a benzamido or naphthamido group, and a substituted arylamido group also typically includes an alkyl-substituted benzamido group such as a p-t-butylbenzamido or p-methylbenzamido group, an alkoxy-substituted benzamido group such as a p-methoxybenzamido or o-dodecyloxybenzamido group, an amido-substituted benzamido group such as a p-acetamidobenzamido, m-lauroylamidobenzamido or m-(2,4-di-t-amylphenoxyacetamido)benzamido group, and a sulfonamido-substituted benzamido group such as an o-hexadecanesulfonamidobenzamido or p-butanesulfonamidobenzamido group.

The alkoxy-carbonylamino group includes a substituted or unsubstituted alkoxy-carbonylamino group having 1 to 22 carbon atoms. It typically includes groups such as ethoxycarbonylamino, i-propoxycarbonylamino, octyloxycarbonylamino, decyloxycarbonylamino, and methoxyethoxycarbonylamino. The aryloxycarbonyl group typically includes a phenoxy-carbonyl group.

The dialkylcarbamoylemino group typically includes groups such as dimethylcarbamoylemino and diethylcarbamoylemino.

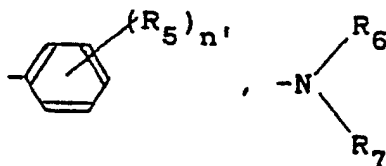
The alkoxy-sulfonamido group includes an unsubstituted alkylsulfonamido group having 1 to 22 carbon atoms, such as a methanesulfonamido, butanesulfonamido or dodecanesulfonamido group, and a substituted alkylsulfonamido group such as a benzylsulfonamido group.

The arylsulfonamido group includes an unsubstituted arylsulfonamido group such as a benzenesulfonamido or naphthalenesulfonamido group, or a substituted arylsulfonamido group including an alkyl-substituted benzenesulfonamido group such as a p-toluenesulfonamido, 2,4,6-trimethylbenzenesulfonamido or p-dodecylbenzenesulfonamido group, and an alkoxy-substituted benzenesulfonamido group such as a p-dodecyloxybenzenesulfonamido or butyloxybenzenesulfonamido group.

A typical example of the sulfamoylamino group preferably includes a dialkylsulfamoylamino group such as a dimethylsulfamoylamino or dibutylsulfamoylamino group.

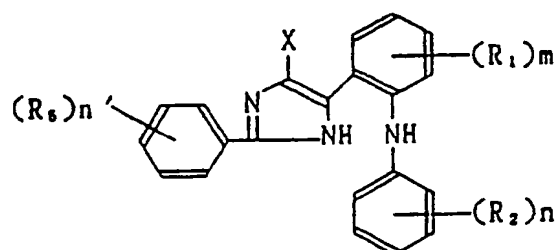
The group represented by X, capable being split off upon coupling reaction with an oxidized product of a color developing agent, includes a halogen atom such as chlorine, bromine or fluorine, and groups such as hydroxyl, alkoxy, aryloxy, heterocyclic oxy, acyloxy, sulfonyloxy, alkoxy-carbonyloxy, aryloxy-carbonyl, alkoxy-oxalyloxy, alkoxy-oxalyloxy, alkylthio, mercapto, arylthio, heterocyclic thio, alkoxy-thiocarbonylthio, acylamino, substituted amino, nitrogen-containing heterocyclic ring combined with a nitrogen atom, sulfonamido, alkoxy-carbonylamino, aryloxy-carbonylamino, and carboxyl. Halogen atom, particularly chlorine atom, is preferable.

Of the compound represented by Formula (I), ones each having a group of;

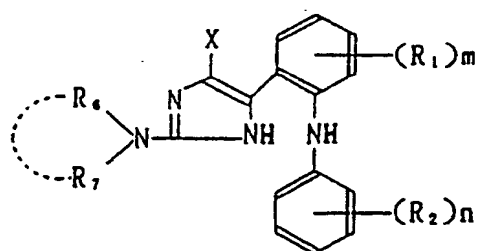


or $-LR_8$ as the group represented by B, namely, represented by Formulas (II), (III) and (IV), are preferably used.

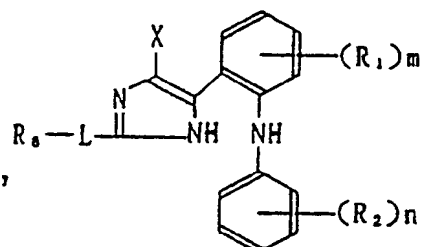
Formula (II)



Formula (III)

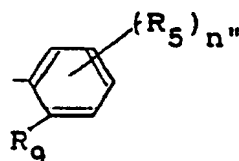


Formula (IV)



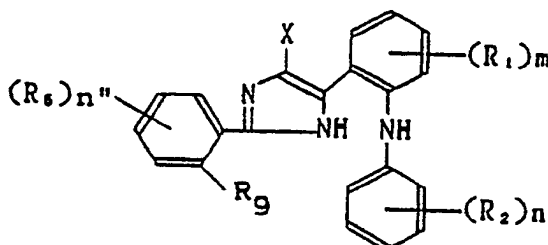
In Formulas (II) to (IV), R_1 , R_2 , X , m and n have the same definitions as R_1 , R_2 , X , m and n in the above Formula (I); R_5 , R_6 , R_7 and R_8 each represent a substituent; L represents an oxygen atom or a sulfur atom; and n' represents an integer of 0 to 5. R_5 may represent different two or more groups when n' is two or more.

Of the compound represented by Formula (II), a still preferred compound includes the compound represented by the following Formula (V), namely, having a



group as the group represented by B.

Formula (V)



In Formula (V), R_1 , R_2 , R_5 , X , m and n have the same definitions as R_1 , R_2 , R_5 , X , m and n in the above Formula (II). n is an integer of zero to 4. R_9 represents an amino group, an alkylamino group, an arylamino group, an alkylamido group, an arylamido group, an alkylsulfonamido group, an arylsulfonamido group, a dialkylcarbamoyl group, an alkoxycarbonylamino group, an aryloxycarbonylamino group or a sulfamoylamino group.

An alkyl group contained in the alkylamino group represented by R_9 may preferably include a straight-chain or branched alkyl group having 1 to 32 carbon atoms, also including a cycloalkyl group such as a cyclohexyl group. These alkyl groups may also be substituted. Preferred substituents typically include a halogen atom, a hydroxyl group, a carboxyl group, a cyano group, a sulfo group, and an alkoxy group having 1 to 22 carbon atoms.

An aryl group contained in the arylamino group represented by R_9 may preferably include a phenyl group. The phenyl group may be substituted with a nitro group, an amido group, a sulfonamido group, or the like.

In instances in which $-R_9$ is an alkylamido group, an arylamido group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a dialkylcarbamoylamino group, an alkylsulfonamido group or an arylsulfonamido group, these groups are the same as the groups represented by R_1 and R_2 in Formula I.

In Formula (III), the alkyl group and aryl group each represented by R_6 or R_7 specifically include the alkyl group and aryl group described for R_9 in the above Formula (V).

The heterocyclic ring formed by combination of R_6 with R_7 may preferably include a heterocyclic ring of 5 or 6 members. These heterocyclic rings may have a substituent, or may further be condensed with a carbon ring.

In Formula (IV), R_8 represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. The alkyl group and aryl group each represented by R_8 specifically include the alkyl group and aryl group described for R_9 in the above Formula (V).

The heterocyclic group represented by R_8 may preferably include a heterocyclic group of 5 or 6 members, specifically including groups such as 2-pyridyl, 4-pyridyl, 2-benzimidazolyl, 3,5-dimethyl-1-pyrazolyl, 4-morpholino, 3,5-dimethyl-2-furyl, 2,4-dimethyl-5-thiazolyl, and 2-acetamido-4-methyl-5-pyrimidinyl.

Typical examples of the cyan coupler used in the present invention are shown below, but the present invention is by no means limited by these.

5

10

15

20

25

30

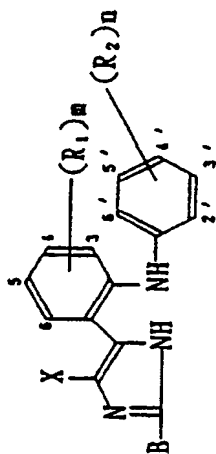
35

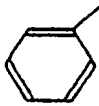
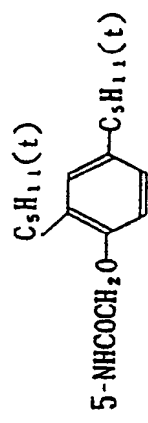
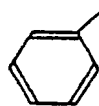
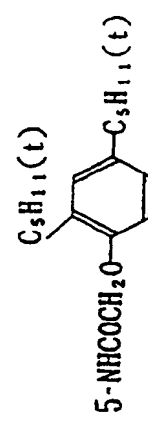
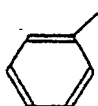
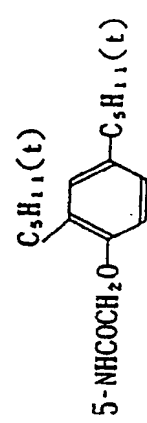
40

45

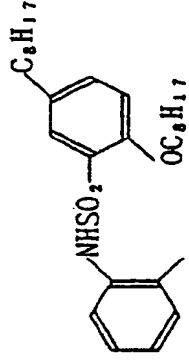
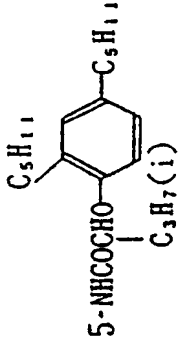
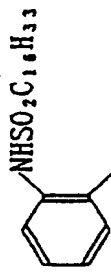
50

55



No.	X	B	R ₁	R ₂	m	n
1	H		 5-NHCOCH ₂ O-C ₆ H ₄ -C ₅ H ₁₁ (t)	—	1	0
2	Cl		 5-NHCOCH ₂ O-C ₆ H ₄ -C ₅ H ₁₁ (t)	—	1	0
3	Cl		 5-NHCOCH ₂ O-C ₆ H ₄ -C ₅ H ₁₁ (t)	2'—Br 4'—Br	1	2

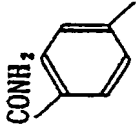
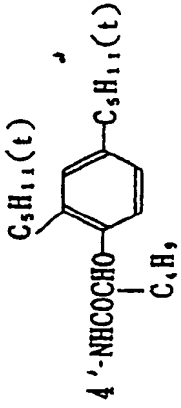
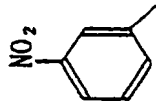
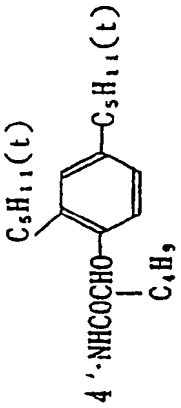
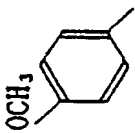
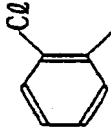
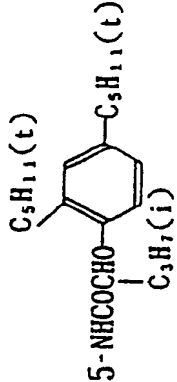
No.	X	B	R ₁	R ₂	m	n
4	H		—	—	0	0
5	Cl		—	—	0	0
6	H		—	—	0	0
7	Cl		—	—	0	0

No.	X	B	R ₁	R ₂	m	n
8	H		5-NHCOCF ₃	—	1	0
9	H		5-NHCOCH ₃	—	1	0
10	Cl			—	1	0
11	Cl		5-NHCOCH ₂ H ₇ (i)	—	1	0

No.	X	B	R ₁	R ₂	m	n
12	C ₂		5-NHCOC ₃ H ₇ (i)	4'-OCH ₃	1	1
13	C ₂			4'-CH ₃	1	1
14				—	1	0
15	H			—	1	0

No.	X	B	R ₁	R ₂	m	n
16	H		5-NHSO ₂ C ₁₆ H ₃₃	—	1	0
17	H			—	1	0
18	C ₂			—	1	0
19	C ₂			3'-CH ₃	1	1

No.	X	B	R ₁	R ₂	m	n
20	Cl		5-NHCOCH ₂ CHC ₄ H ₉ C ₂ H ₅	—	1	0
21	Cl		5-NHCOCHO C ₄ H ₉ C ₅ H ₁₁ (t) C ₅ H ₁₁ (t)	4'-NHCOCH ₃	1	1
22	H	CH ₃ O—	—	4'-NHCOCHO C ₃ H ₇ (i) C ₅ H ₁₁ (t) C ₅ H ₁₁ (t)	0	1
23	Cl	CH ₃ O—	5-NHCOCHO C ₄ H ₉ C ₅ H ₁₁ (t) C ₅ H ₁₁ (t)	2'-Cl 4'-Cl	1	2

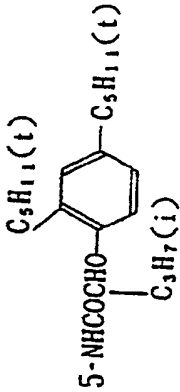
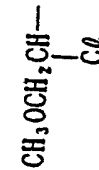
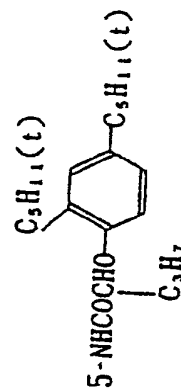
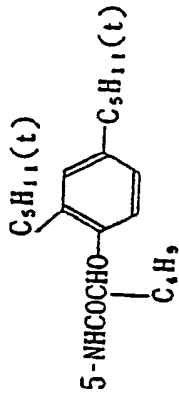
No.	X	B	R ₁	R ₂	m	n
24	H		—		0	1
25	H		—		0	1
26	Cl		$5\text{-NHCOCHCH}_2\text{SO}_2\text{C}_{12}\text{H}_{25}$ CH ₃	—	1	0
27	H			$2'\text{-Br}$ $4'\text{-Br}$	1	2

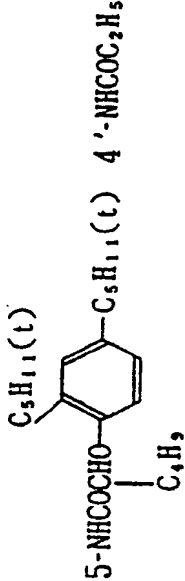
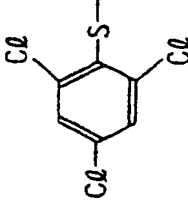
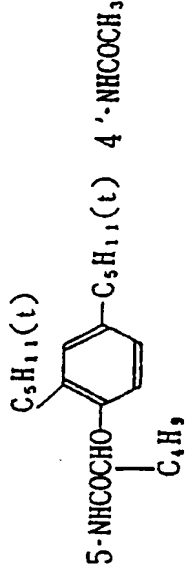
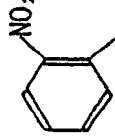
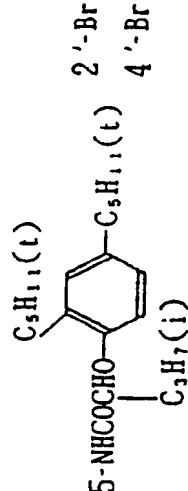
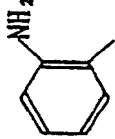
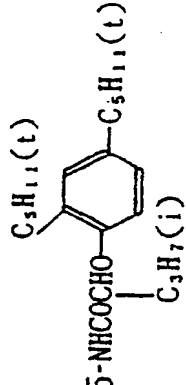
No.	X	B	R ₁	R ₂	m	n
28	H			2'-Br 4'-Br	1	2
29	H			—	1	0
30	H			2'-Br 4'-Br	1	2
31	H			—	1	0

No.	X	B	R ₁	R ₂	m n
32	H			—	1 0
33	C ₀			—	1 0
34	H			—	1 0
35	C ₀			—	1 0

No.	X	B	R ₁	R ₂	m	n
36	Cl				1	1
37	Cl				1	1
38	Cl				1	1
39	H			—	1	0

No.	X	B	R ₁	R ₂	m	n
40	H			—	1	0
41	H	(t)C ₈ H ₁₇ NH—	5-NHCOOCH ₂ CHC ₄ H ₉ C ₂ H ₅	—	1	0
42	Cl	C ₁₆ H ₃₃ S—	5-NHCOOC ₃ H ₇ (i)	—	1	0
43	Cl			—	1	0

No.	X	B	R_1	R_2	m	n
44	Cl	$CH_3SO_2NHCH_2CH_2S-$	5-NHCOC ₂ H ₅	4'-NHCOC ₁₁ H ₂₃	1	1
45	Cl	(i)C ₃ H ₇ O-		4'-Cl	1	1
46	Cl			4'-Cl	1	1
47	Cl	ClCH ₂ -		2'-Cl 4'-Cl	1	2

No.	X	B	R ₁	R ₂	m	n
48	Cl	C ₁₈ H ₃₃ S—		4'-NHCOCH ₂ H ₅	1	1
49	H			4'-NHCOCH ₃	1	1
50	H			2'-Br 4'-Br	1	2
51	H			—	1	0

No.	X	B	R ₁	R ₂	m	n
52	H			—	1	0
53				—	1	0
54				—	1	0

Typical examples for synthesizing the coupler of the present invention are described below.

Synthesis Example 1 (Synthesis of Exemplary Compound 30)

Synthesis of 2-chloro-5-nitroacetophenone

On a ice bath, 80 ml of fuming nitric acid ($d = 1.52$) was cooled to 4°C , and 24.0 g of o-chloroacetophenone was dropwise added thereto at 4 to 7°C taking about 3 hours. In the state as it stands, stirring was continued at 4°C for 1 hour.

The reaction mixture was subsequently poured onto ice, and pale yellow crystals deposited were collected by filtration. The crystals were recrystallized from alcohol to obtain 22 g of 2-chloro-5-

nitroacetophenone.
m.p.: 59 to 61 °C.

5 Synthesis of 2-acetyl-4-nitrodiphenylamine

Under heating at 125 °C to 135 °C, 20 g of 2-chloro-5-nitroacetophenone, 20 g of aniline and 20 g of anhydrous potassium carbonate were stirred for 5 hours.

When cooled to about 80 °C, 80 ml of alcohol was added and the reaction mixture was allowed to cool with stirring. After it was allowed to stand overnight in that state, yellowish brown crystals were deposited. The crystals were collected by filtration, washed with alcohol, and then washed with water. The resulting crude crystals were recrystallized from alcohol to obtain 11.0 g of 2-acetyl-4-nitrodiphenylamine.
m.p.: 130 to 132 °C

15 Synthesis of 2-acetyl-4-{2-(2'-4'-di-t-amylphenoxy-i-pentanamido)}diphenylamine

In a mixture of 10.2 g of 2-acetyl-4-nitrodiphenylamine and 200 ml of alcohol, 0.5 g of a Pd-C catalyst was added to carry out catalytic reduction at normal pressure. In about 3 hours, 2.8 l of hydrogen was absorbed and the reduction stopped (theoretical quantity: 1.35 l). The reaction mixture turned thick yellow.

The catalyst was removed by filtration, and the filtrate was concentrated. The remaining yellowish brown oil was stood under a reduced pressure made by a vacuum pump for removing the remaining alcohol in the oil, which thus obtained oily substance was used for the next reaction as it was.

The oily substance previously mentioned was dissolved in 200 ml of acetonitrile, and then 4.0 g of pyridine was added. Into this mixture, poured was a solution obtained by dissolving 14.1 g of 2,4-di-t-amylphenoxy-i-pentanoylchloride in 50 ml of acetonitrile. Heat was generated and crystals were formed, which, however, were dissolved after a while as a result of stirring. The resulting solution was boiled and refluxed for 2 hours, and thereafter concentrated.

The remaining viscous substance was extracted with ethyl acetate, and the ethyl acetate layer was washed with diluted hydrochloric acid, and then washed with water, followed by dehydration with magnesium sulfate.

The ethyl acetate layer was concentrated, and the remaining oil was purified by column chromatography. There was obtained 22.0 g of a yellow amorphous solid.

35 Synthesis of Exemplary Compound 30

In 150 ml of chloroform, 11.1 g of 2-acetyl-4-{2-(2'-4'-di-t-amylphenoxy-i-pentanamido)}diphenylamine was dissolved. To the resulting solution, 9.85 g of bromine was dropwise added taking about 3 hours at room temperature. The reaction mixture was further maintained at room temperature for 30 minutes, and thereafter for 30 minutes at temperatures raised to 40 to 50 °C, followed by concentration after completion of the reaction. The remaining yellowish brown oil was again dissolved in 200 ml of chloroform. In the resulting solution, a chloroform solution of 3,5-dimethylpyrazolecarboamidinium⁺ (prepared from 16.5 g of a nitrate thereof) was added with stirring, and the mixture was boiled and refluxed for 10 hours. Deposition of crystals followed. Since, however, the crystals were comprised of 3,5-dimethylpyrazolecarboamidinium nitrate, they were removed by filtration after the reaction, and the resulting filtrate was concentrated. The remaining oil content was separated and purified by column chromatography, thus obtaining 13.4 g of Exemplary Compound 30 as an amorphous solid.

Mass spectrometry confirmed that this product showed $M^+ = 818$ and had the structure as previously set out.

* In 50 ml of water, 16.5 g of 3,5-dimethylpyrazolecarboamidinium nitrate was added and almost completely dissolved, following by addition, with stirring, of a solution obtained by dissolving 33 g of potassium hydroxide in 50 ml of water. Free carboamidinium, separated as an oil, was extracted with chloroform. The liquid chloroform extract was dehydrated using anhydrous magnesium sulfate, and the resulting solution was used in the reaction as it was.

Synthesis Example 2 (Synthesis of Exemplary Compound 34)

In 5.92 g of Exemplary Compound 30, 160 ml of alcohol, 1.82 g of triethylamine and also a Raney nickel catalyst, and the mixture was subjected to catalytic reduction at normal pressure for 32 hours. Formation of white precipitates followed with progress of the reaction. After the reaction was completed, the resulting white crystals were collected by filtration and then washed with alcohol. To separate them from the Raney nickel catalyst, the crystals obtained were treated with an aqueous diluted ammonium solution and extracted with ethyl acetate. The ethyl acetate layer was dehydrated with anhydrous magnesium sulfate, followed by concentration. The remaining grayish white solid was recrystallized from acetonitrile to obtain 2.4 g of Exemplary Compound 34.

m.p.: 184.5 to 186.5 °C

Synthesis Example 3 (Synthesis of Exemplary Compound 35)

In a mixture of 30 ml of ethyl acetate and 50 ml of dimethylformamide, 2.0 g of the above Exemplary Compound 34 was dissolved, to which 0.44 g of N-chlorosuccinimide was added, and then the reaction was carried out at room temperature for 3 days. The reaction product was poured onto water, and extracted with ethyl acetate. The resulting ethyl acetate layer was washed with water and thereafter dehydrated with anhydrous magnesium sulfate, followed by concentration. The remaining pale brown oil was purified by column chromatography to obtain 1.1 g of a pale brown amorphous solid.

Mass spectrometry confirmed that this product showed $M^+ = 694$ and was identified to be the intended product.

Synthesis Example 4 (Synthesis of Exemplary Compound 50)

Using 6.76 g of o-nitrobenzamidine in place of the 3,5-dimethylpyrazolecarboamidine in the synthesis of Exemplary Compound 30, the reaction was carried out similarly, followed by purification by column chromatography to obtain 2-(o-nitrophenyl)-4-[2-(2',4'-dibromoanilino)-5-{2'-(2'',4''-di-t-amylphenoxy-i-pentanamido)}phenyl]imidazole as a reddish brown amorphous solid. Yield: 8.7 g

Synthesis Example 5 (Synthesis of Exemplary Compound 51)

In 7.0 g of the above 2-(o-nitrophenyl)-4-[2-(2',4'-dibromoanilino)-5-{2'-(2'',4''-di-t-amylphenoxy-i-pentanamido)}phenyl]imidazole, 60 ml of tetrahydrofuran, 60 ml of ethanol and 0.6 g of a Pd-C catalyst were added to carry out catalytic reduction at normal pressure. The reduction was completed after about 5 days. The catalyst was removed by filtration, and the filtrate was concentrated to obtain 5.46 g of a grayish white solid.

Mass spectrometry of this product showed $M^+ = 657$ and substantiated the structure of 2-(o-aminophenyl)-4-[2-anilino-5-{2'-(2'',4''-di-t-amylphenoxy-i-pentanamido)}phenyl]imidazole.

Synthesis Example 6 (Synthesis of Exemplary Compound 52)

In 4.2 g of the above Exemplary Compound 51, 40 ml of acetonitrile was added, and 2.52 g of 2-octyloxy-5-octylbenzenesulfonyl chloride as further added, followed by stirring. In the resulting reaction mixture, 0.6 g of pyridine was added, and thereafter the reaction was carried out at room temperature for about 3 hours.

With addition of water, the reaction product was extracted with ethyl acetate. The ethyl acetate layer was washed with diluted hydrochloric acid, next with water, and further with diluted ammonia water. Thereafter it was again washed with water and dehydrated with magnesium sulfate. The ethyl acetate layer was concentrated, and the remaining viscous product was recrystallized from acetonitrile to obtain 3.78 g of white crystals.

m.p.: 184 to 186 °C.

Synthesis Example 7 (Synthesis of Exemplary Compound 10)

In 100 ml of ethyl acetate, 3.28 g of Exemplary Compound 52 obtained in Synthesis Example 6 was dissolved, to which 0.52 g of N-chlorosuccinimide was added with stirring to effect dissolution. The reaction mixture was left to stand as it was, at room temperature for 3 weeks. Thereafter, water was added to separate an ethyl acetate layer. The ethyl acetate layer was dehydrated and then concentrated to obtain 3.5 g of a viscous product. The product was purified by column chromatography, and the viscous product that turned 2.1 g was stood in a reduced pressure to obtain an amorphous solid.

Mass spectrometry confirmed that this product showed $M^+ = 1,071$ and was identified to be Exemplary Compound 10.

Synthesis Example 8 (Synthesis of Exemplary Compound 17)

Synthesis Example 6 was repeated to carry out the reaction, except that 0.82 g of ethyl chloroformate was used in place of 2-octyloxy-5-octylbenzenesulfonyl chloride. The reaction product was purified by column chromatography to obtain 3.6 g of an amber viscous product. Mass spectrometry of this product showed $M^+ = 729$ and substantiated the structure of Exemplary Compound 17.

In the silver halide photographic light-sensitive material of the present invention, the cyan coupler of the present invention may preferably be added in an amount of from 10 to 300 g per mol of silver halide, which amount can be optionally varied in an appropriate range.

The coupler of the present invention can be used in combination of two or more couplers, or can be used in combination with a different type of cyan coupler.

The coupler of the present invention can be added in the silver halide photographic light-sensitive material by use of various methods such as a solid dispersion method, a latex dispersion method, and an O/W emulsifying dispersion method. For example, the O/W emulsifying dispersion method may be carried out usually by dissolving hydrophobic additives such as couplers in a high-boiling organic solvent having a boiling point of not less than about 150°C such as tricresyl phosphate or dibutyl phthalate, optionally together with a low-boiling solvent such as ethyl acetate and butyl propionate and/or water-soluble organic solvent, subjecting the resulting solution to emulsification dispersion in a hydrophilic binder such as an aqueous gelatin solution with use of a surface active agent, and thereafter adding the resulting dispersion to an intended hydrophilic colloid layer.

The silver halide photographic light-sensitive material of the present invention can be applied, for example, in color negative, positive or reversal films, and color photographic papers.

The silver halide photographic light-sensitive material of the present invention, including the color films, may have the structure that a green-sensitive emulsion layer, a red-sensitive emulsion layer and a blue-sensitive emulsion layer containing, respectively, a magenta coupler, a cyan coupler of the invention and a yellow coupler, and a non-light-sensitive layer, are laminated on a support in an appropriate layer number and layer order. The layer number and layer order, however, may be appropriately changed depending on the performance to be emphasized and the purpose for which the light-sensitive material is used.

In silver halide emulsions used in the silver halide photographic light-sensitive material of the present invention, any silver halides may be used, including silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide and silver chloride, which are used in usual silver halide emulsions.

The silver halide emulsions may be chemically sensitized by the processes as exemplified by sulfur sensitization, selenium sensitization, reduction sensitization, and noble metal sensitization. The silver halide emulsions may also be optically sensitized to a desired wavelength region by using dyes known as sensitizing dyes in the field of photographic industries.

In the silver halide photographic light-sensitive material of the present invention, it is possible to optionally use anti-color-fogging agents, hardening agents, plasticizers, polymer latexes, ultraviolet absorbers, formalin scavengers, mordants, development accelerators, development restrainers, fluorescent whitening agents, matting agents, lubricants, antistatic agents, and surface active agents.

In the present invention, any processing used in the present industrial field can be carried out, as exemplified by the processing such as color developing, bleaching, fixing or bleach-fixing, stabilizing, washing, and stopping.

The silver halide photographic light-sensitive material of the present invention, which contains the novel cyan coupler, can achieve good spectral absorption characteristics of the cyan dyes formed. Namely, it shows a good sharp cut-off at the shortwave side of the absorption, less unwanted absorption at the green portion and blue portion, and superior color reproducibility. In other words, because of the high color-

forming properties possessed by the cyan coupler of the present invention, it becomes possible to make films thinner to improve the image sharpness. Moreover, the thermal resistance and light-resistance of the dyes formed can be improved.

5

EXAMPLES

Specific examples of the present invention will be described below, but the embodiments of the present invention are by no means limited to these.

Example 1

Based on 0.0126 mol of the cyan coupler as shown in Table 1, 3 g of dibutyl phthalate was added and 18 g of ethyl acetate was further added, thus obtaining a mixture solution. The mixture solution was heated to 60° C and dissolved, and thereafter the resulting solution was mixed into 100 ml of an aqueous 5 % gelatin solution containing 10 ml of an aqueous 5 % solution of Alkanol B (a trademark for an alkyl naphthalene sulfonate, available from DuPont Co.), followed by emulsifying dispersion using an ultrasonic dispersing machine to prepare a dispersion.

The above dispersion was next added in a silver iodobromide emulsion (containing 6 mol % of silver iodide) so that the cyan coupler may be 10 mol % based on the silver. In the resulting solution, 1,2-bis-(vinylsulfonyl)ethane was further added as a hardening agent in a proportion of 12 mg per 1 g of gelatin, followed by coating of the solution on a transparent triacetate cellulose film support so as to give a coated silver weight of 18 mg/100 cm². Each silver halide photographic light-sensitive material thus obtained was subjected to exposure through an optical wedge according to a conventional method, and thereafter the following processing was carried out thereon.

30

Processing steps:	
Processing steps (38° C)	Processing time
Color developing	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec

35

40

The processing solutions used in the processing steps had the following composition.

45

(Color developing solution)	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 l by the addition of water, and adjusted to pH 10.0 using potassium hydroxide.	

55

(Bleaching solution)	
Ammonium ferric ethylenediaminetetraacetate	100 g
Diammonium ethylenediaminetetraacetate	10 g
Ammonium bromide	150 g
Glacial acetic acid	10 ml
Made up to 1 l by the addition of water, and adjusted to pH 6.0 using ammonia water.	

(Fixing solution)	
Ammonium thiosulfate (an aqueous 50 % solution)	162 ml
Anhydrous sodium sulfite	12.4 g
Made up to 1 l by the addition of water, and adjusted to pH 6.5 using acetic acid.	

(Stabilizing solution)	
Formalin (an aqueous 37 % solution)	5.0 ml
Konidax (a product of Konica Corporation)	7.5 ml
Made up to 1 l by the addition of water.	

On the silver halide photographic light-sensitive materials thus obtained, the fog, speed S_1 , and maximum density D_{max} of cyan dye images were measured.

Results obtained are shown in Table 1.

Table 1

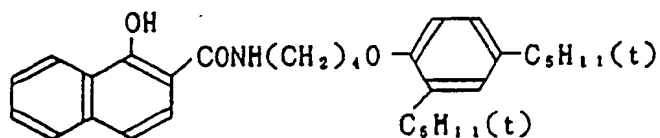
Sample			Fog	S_1	Dmax
	No.	Coupler			
1 (X)	C-1*		0.14	100	1.45
2 (Y)	Exemplary 1		0.12	108	1.63
3 (")	"	4	0.13	107	1.65
4 (")	"	9	0.14	110	1.70
5 (")	"	29	0.14	108	1.68
6 (")	"	30	0.13	111	1.75
7 (")	"	34	0.11	113	1.75
8 (X)	C-2*		0.25	130	2.10
9 (Y)	Exemplary 2		0.20	150	2.15
10 (")	"	5	0.23	163	2.20
11 (")	"	10	0.22	170	2.28
12 (")	"	18	0.24	165	2.25
13 (")	"	23	0.24	185	2.30
14 (")	"	35	0.23	160	2.20
15 (")	"	42	0.21	162	2.25

X: Comparative Example

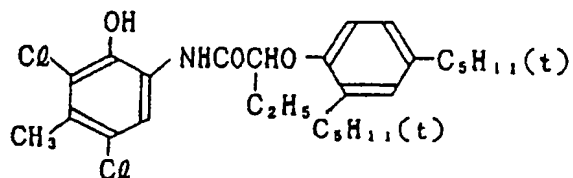
Y: Present Invention

* Comparative coupler:

C - 1



C - 2



In the Table 1, inventive Samples 2 to 7 should be compared with comparative Sample 1, which samples each contain 2-equivalent groups. Samples 9 to 15 are comparable with comparative Sample 8, which samples each contain 4-equivalent couplers.

As will be evident from Table 1, all the couplers of the present invention have higher color-forming properties than the conventional couplers.

Example 2

(Preparation of silver halide emulsion)

Six kinds of silver halide emulsions as shown in Table 2 were prepared according to a neutral method and a simultaneous mixing method.

Table 2

Emulsion No.	AgCl mol %	AgBr mol %	Average grain size (μm)	Chemical sensitizer	Spectral sensitizing dye
Em-1	99.5	0.5	0.67	Sodium thiosulfate ^{*1} & chloraurate ^{*2}	SD-1 ^{*3}
Em-2	99.5	0.5	0.46		SD-2 ^{*4}
Em-3	99.5	0.5	0.43		SD-3 ^{*5}
Em-4	10	90	0.67	Sodium thiosulfate ^{*1}	SD-1 ^{*3}
Em-5	30	70	0.46		SD-2 ^{*4}
Em-6	30	70	0.43		SD-3 ^{*5}

^{*1}: In an amount of 2 mg per mol of silver halide.

^{*2}: In an amount of 5×10^{-5} mol. per mol of silver halide.

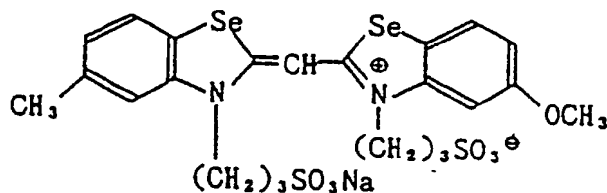
^{*3}: In an amount of 0.9 mmol per mol of silver halide.

^{*4}: In an amount of 0.7 mmol per mol of silver halide.

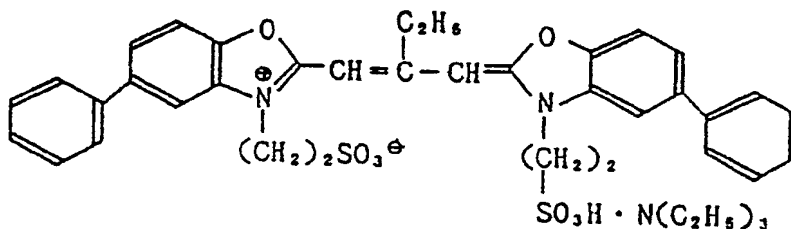
^{*5}: In an amount of 0.2 mmol per mol of silver halide.

After the respective silver halide emulsions were chemically sensitized, the following STB-1 was added as an emulsion stabilizer in an amount of 5×10^{-3} mol per mol of silver halide.

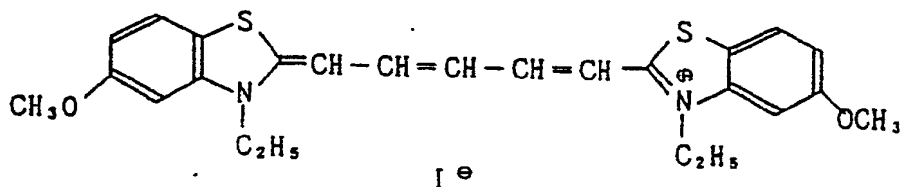
[SD - 1]



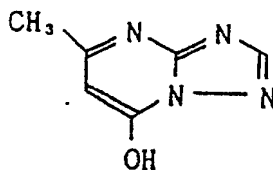
[SD - 2]



[SD - 3]



[STB - 1]



(Preparation of silver halide color photographic light-sensitive material)

Subsequently, the following Layers 1 to 7 were successively provided by coating on paper supports covered on their both sides with polyethylene, to prepare silver halide color photographic light-sensitive materials Samples 16 to 22. In the following examples, the amount for addition is indicated as an amount per 1 m² of a light-sensitive material.

Layer 1:

A layer containing 1.2 g of gelatin, 0.29 g (in terms of silver; the same applies hereinafter) of a blue-sensitive silver halide emulsion (Em-1) and 0.3 g of dinonylphthalate in which 0.75 g of a yellow coupler (Y-1), 0.3 g of a light stabilizer ST-1 and 0.015 g of 2,5-diethylhydroquinone (HQ-1) were dissolved.

Layer 2:

A layer containing 0.9 g of gelatin and 0.2 of DOP (dioctylphthalate) in which 0.04 g of HQ-1 was dissolved.

Layer 3:

A layer containing 1.4 g of gelatin, 0.2 g of a green-sensitive silver halide emulsion (Em-2), 0.3 g of dioctylphthalate in which 0.50 g of a magenta coupler (M-1), 0.25 g of a light stabilizer (ST-2) and 0.01 g of HQ-1 were dissolved, and 6 mg of the following filter dye (Al-1).

Layer 4:

A layer containing 1.2 g of gelatin and 0.3 g of DNP in which 0.6 g of the following ultraviolet absorbent (UV-1) and 0.05 g of HQ-1 were dissolved.

Layer 5:

A layer containing 1.4 g of gelatin, 0.20 g of a red-sensitive silver halide emulsion (Em-3) and 0.3 g of DOP in which 0.9 mmol of the cyan coupler as shown in Table 3 and 0.01 g of HQ-1 were dissolved.

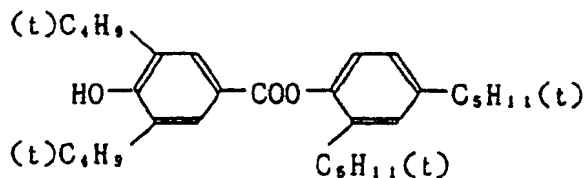
Layer 6:

A layer containing 1.1 g of gelatin, 0.2 g of DOP in which 0.2 g of UV-1 was dissolved, and 5 mg of the following filter dye (Al-2).

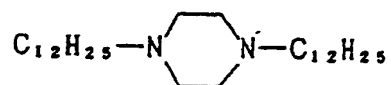
Layer 7:

A layer containing 1.0 g of gelatin and 0.05 g of sodium 2,4-dichloro-6-hydroxytriazine.

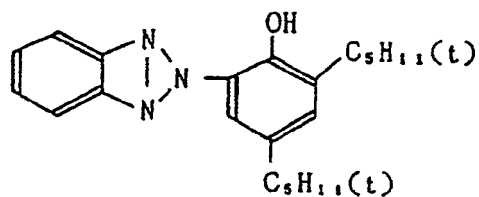
(ST-1)



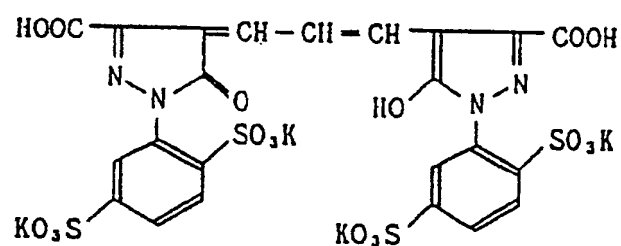
(ST-2)



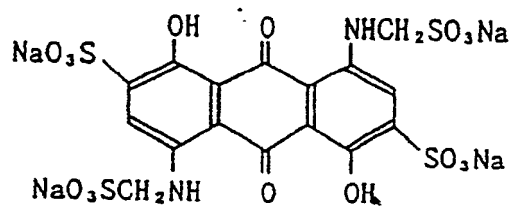
(UV-1)



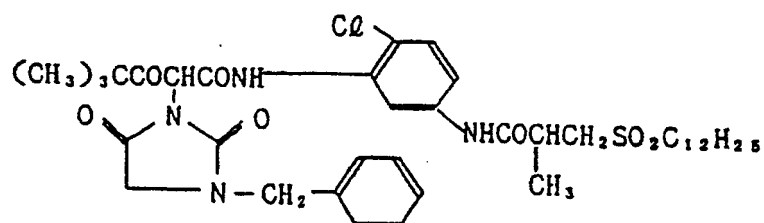
(AI-1)



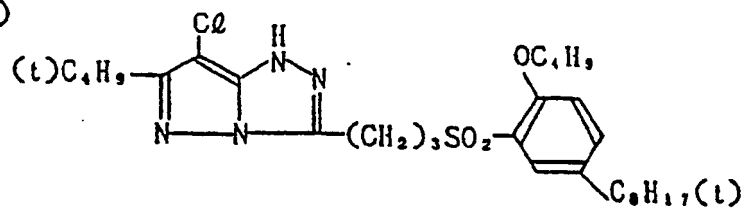
(AI-2)



(Y-1)



(M-1)



The samples obtained were subjected to exposure through an optical wedge, using a sensitometer Type KS-7 (available from Konica Corporation), followed by processing according to the following color developing processing steps. Thereafter, an optical densitometer Type PDA-65 (available from Konica Corporation) was used to measure the speed (a reciprocal of the amount of exposure that gives a density of fog + 0.1) and maximum density (Dmax) of red-sensitive emulsion layers.

The samples obtained were also stored at 85 °C under a relative humidity of 60 % for 20 days, and the remaining ratio (%) of dye images at the initial density 1.0 was determined to evaluate dark color-fading properties. Results obtained are shown in Table 3.

Processing steps:		
	Temperature	Time
Color developing	34.7 ± 0.3 °C	45 sec
Bleach-fixing	34.7 ± 0.3 °C	50 sec
Stabilizing	30 to 34 °C	90 sec
Drying	60 to 80 °C	60 sec

(Color developing solution)	
Pure water	800 ml
Triethanolamine	8 g
N,N-diethylhydroxylamine	5 g
Potassium chloride	2 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5 g
Sodium tetrapolyphosphate	2 g
Potassium carbonate	30 g
Potassium sulfite	0.2 g
Fluorescent whitening agent (a 4,4'-diaminostilbenedisulfonic acid derivative)	1 g
Made up to 1 l in total amount by the addition of pure water, and adjusted to pH 10.2.	

(Bleach-fixing solution)	
Ammonium ferric ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (a 70 % solution)	100 ml
Ammonium sulfite (a 40 % solution)	27.5 ml
Made up to 1 l in total amount by the addition of water, and adjusted to pH 5.7 using potassium carbonate or glacial acetic acid.	

(Stabilizing solution)	
5-Chloro-2-methyl-4-isothiazolin-3-on	1 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2 g
Made up to 1 l by the addition of water, and adjusted to pH 7.0 using sulfuric acid or potassium hydroxide.	

Comparative coupler (C-3)

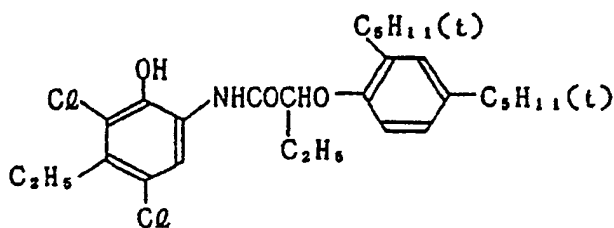


Table 3

Sample No.	Coupler	Speed*	Dmax	Remaining
				ratio of color image
16 (X)	C-2	100	2.55	80 %
17 (")	C-3	97	2.55	92
18 (Y)	Exemplary 10	115	2.63	94
19 (")	" 18	110	2.66	95
20 (")	" 35	112	2.65	94
21 (")	" 37	110	2.61	96
22 (")	" 38	108	2.62	95

X: Comparative Example

Y: Present Invention

* The speed is indicated by a relative value, assuming

the speed of Sample 16 as 100.

As is evident from Table 3, a high maximum density and a high speed can be obtained and also the resulting cyan images have a good thermal resistance, when the cyan couplers of the present invention are used.

The color reproducibility was also visually evaluated on the samples obtained by printing the above Samples 16, 17, 20, 21, 22 through color negatives obtained by photographing Color Checker (available from Macbeth Co.) using Konicolor GX-100 under conditions adjusted so that the image of neutral color portion of Color Checker is reproduced to neutral color on the printed samples.

When compared with Samples 16 and 17, Samples 20, 21 and 22, which are in accordance with the present invention, have been remarkably improved in the distinction between blue and cyan and the color reproducibility of green and red to magenta.

5

Example 3

Example 2 was entirely repeated to prepare silver halide photographic light-sensitive materials Samples 23 to 29, except that the blue-sensitive silver halide emulsion used in Layer 1, the green-sensitive silver halide emulsion used in Layer 3 and the red-sensitive silver halide emulsion used in Layer 5 were respectively replaced with Em-4, Em-5 and Em-6 shown in Table 2.

The samples obtained were subjected to exposure through an optical wedge, using a sensitometer Type KS-7 (manufactured by Konica Corporation), followed by processing according to the following color development processing steps. Thereafter the same measurement as Example 2 was made.

Results obtained are shown in Table 4.

20

(Processing steps)		
Color developing	3 min 30 sec	Temp: 33 ° C
Bleaching	1 min 30 sec	Temp: 33 ° C
Washing	3 min	Temp: 33 ° C

25

30

35

Color developing solution	
N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.9 g
Hydroxylamine sulfate	2.0 g
Potassium carbonate	25.0 g
Potassium bromide	0.6 g
Anhydrous sodium sulfite	2.0 g
Benzylalcohol	13 ml
Polyethylene glycol	3.0 ml
(average degree of polymerization: 400)	
Made up to 1 l by the addition of water, and adjusted to pH 10.0 using sodium hydroxide.	

40

Bleach-fixing solution

45

50

55

Sodium ferric ethylenediaminetetraacetic acid 6.0 g

Ammonium thiosulfate 100 g

5 Sodium bisulfite 10 g

Sodium metabisulfite 3 g

10 Made up to 1 l by the addition of water, and adjusted to pH 7.0 using ammonia water.

15

Table 4

Sample No.	Coupler	Speed*	Dmax	Remaining ratio of color image
23 (X)	C-2	100	2.50	81 %
24 (")	C-3	101	2.52	91
25 (Y)	Exemplary 10	118	2.68	93
26 (")	" 18	113	2.66	92
25 27 (")	" 35	110	2.70	94
28 (")	" 37	115	2.71	95
29 (")	" 38	117	2.68	95
X: Comparative Example				
Y: Present Invention				

30

* The speed is indicated by a relative value, assuming the speed of Sample 23 as 100.

35

Example 4

40 The following emulsions were prepared.

Preparation of Emulsion S:

45 A 2.0 % inert gelatin solution (750 ml) was maintained at 50° C, and the following Solutions A1 and B were simultaneously added therein with stirring, which were poured into it taking 3 minutes. After ripening for 25 minutes, excessive salts were removed by precipitation washing. The resulting flocculate was redispersed, followed by addition of Solutions C1 and D1. After 10 minutes, excessive water-soluble salts were again removed, a small amount of gelatin was added, and then the silver halide particles were
50 dispersed.

Preparation of Emulsion L:

55 A 1.5 % inert gelatin solution (750 ml) was maintained at 60° C, and the following Solutions A2 and B were simultaneously added therein with stirring, which were poured into it taking 15 minutes. After ripening for 40 minutes, excessive salts were removed by precipitation washing. The resulting flocculate was redispersed, and 10 mg of sodium thiosulfate was added, followed by addition of Solutions C2 and D2. After

10 minutes, excessive water-soluble salts were again removed, a small amount of gelatin was added, and then the silver halide particles were dispersed.

5 Preparation of Emulsion M:

A 2.0 % inert gelatin solution (750 ml) was maintained at 50 ° C, and the following Solutions A3 and B were simultaneously added therein with stirring, which were poured into it taking 4 minutes. After ripening for 25 minutes, excessive salts were removed by precipitation washing. The resulting flocculate was redispersed, followed by addition of Solutions C1 and D2. After 10 minutes, excessive water-soluble salts were again removed, a small amount of gelatin was added, and then the silver halide particles were dispersed.

15

Solution A1:	
Pure water	2,000 ml
NaCl	35 g
NH ₄ Br	109.6 g
KI	0.8 g

20

25

Solution A2:	
Pure water	1,000 ml
NaCl	26.3 g
NH ₄ Br	109.6 g
KI	0.8 g

30

35

Solution A3:	
Pure water	1,000 ml
NaCl	33.8 g
KBr	12 g

40

45

Solution B:

50

Pure water	1,200 ml
AgNO ₃	170 g

55

Solution C1:	
Pure water	1,000 ml
NaCl	60 g
NH ₄ Br	6.9 g

Solution C2:	
Pure water	1,000 ml
NaCl	31.6 g

Solution D1:	
Pure water	1,000 ml
AgNO ₃	70 g

Solution D2:	
Pure water	1,000 ml
AgNO ₃	80 g

In the above three types of emulsions, sensitizing dyes, couplers and so forth were added in the following way. The resulting solutions were coated on a support to prepare a multi-layer color light-sensitive material.

Red-sensitive emulsion layer (First layer):

To Emulsions S and M, respectively, added were sensitizing dyes (PD-3) and (PD-4), stabilizers (STB-1) and (STB-2), a surface active agent (S-2), and further a protectively dispersed coupler solution containing dibutyl phthalate, ethyl acetate, a surface active agent (S-2), 2,5-dioctylhydroquinone and cyan couplers (C-2) and (C-4).

Gelatin was added. The respective emulsions were mixed, and the resulting mixed emulsion was coated so that a gamma value of 1.5 may be given.

First intermediate layer (Second layer):

A gelatin solution containing a protectively dispersed solution containing dioctyl phthalate, 2,5-dioctylhydroquinone, an ultraviolet absorbent Tinubin 328 (available from Ciba Geigy Corp.) and a surface active agent (S-1) was prepared, and coated so that Tinubin may be in a coating weight of 0.15 g/m².

Green-sensitive emulsion layer (Third layer):

To Emulsions S and M, respectively, added were a sensitizing dye (PD-2), stabilizers (STB-1) and (STB-2), a surface active agent (S-2), and further a protectively dispersed coupler solution containing dibutyl phthalate, ethyl acetate, 2,5-dioctylhydroquinone, a surface active agent (S-1), and a magenta coupler (M-2).

5 Gelatin was added, and a hardening agent (H-1) was further added. The resulting mixed emulsion was coated so that a gamma value of 1.5 may be given.

Second intermediate layer (Fourth layer):

10

With the same formulation with the first intermediate layer, the solution was coated so that Tinubin 328 may be in a coating weight of 0.2 g/m².

15 Yellow filter layer (Fifth layer):

To an yellow colloidal silver solution prepared by reduction in the presence of an alkaline weakly reducing agent (after neutralization, the weakly reducing agent was removed by noodle washing method), a solution comprising dioctyl phthalate, ethyl acetate, a surface active agent (S-1), and 2,5-dioctylhydroquinone, a surface active agent (S-2) and a hardening agent (H-1) were added. The resulting solution was coated so that the colloidal silver may be in a coating weight of 0.15 g/m².

20

Third intermediate layer (Sixth layer):

25

The same as the first intermediate layer.

Blue-sensitive emulsion layer (Seventh layer):

30

To Emulsions L, S and M, respectively, added were a sensitizing dye (PD-1), stabilizers (STB-1) and (STB-3), a surface active agent (S-2), and further a protectively dispersed coupler solution containing dibutyl phthalate, ethyl acetate, 2,5-dioctylhydroquinone, a surface active agent (S-1), and a yellow coupler (Y-2). Gelatin was added, and a hardening agent (H-1) was further added. The resulting emulsions were mixed and coated so that a gamma value of 1.5 may be given.

35

Third intermediate layer (Eighth layer):

40

With the same formulation as the first intermediate layer, the solution was coated so that Tinubin 328 may be in a coating weight of 0.2 g/m².

Protective layer (Ninth layer):

45

A gelatin solution containing colloidal silica, a surface active agent (S-2) and hardening agents (H-2) and (H-3) was coated so that the gelatin may be in a coating weight of 1.0 g/m².

On a polyethylene-laminated paper having been subjected to surface treatment, the first layer to the ninth layer were provided by a simultaneous coating method, followed by drying (Sample 30).

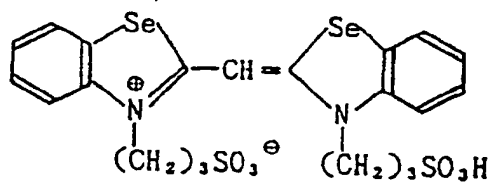
50

Samples 31 to 33 were further prepared in the same manner except that the cyan coupler used in the red-sensitive layer (the first layer) was replaced with equimolar amounts of the couplers of the present invention as shown in Table 5.

55

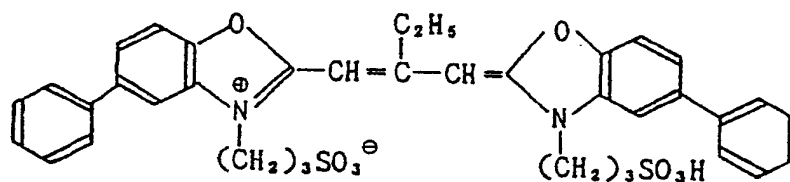
[P D - 1]

5



[P D - 2]

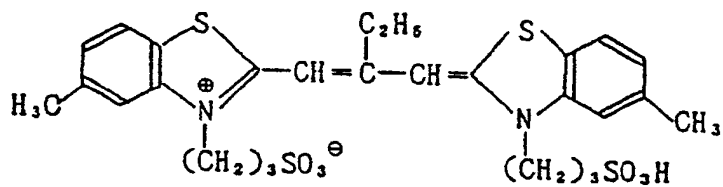
10



15

[P D - 3]

20



25

30

35

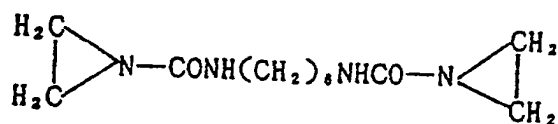
40

45

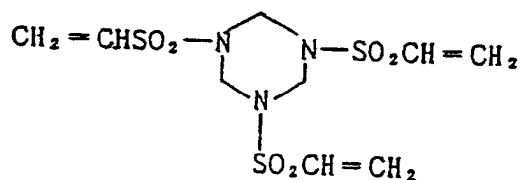
50

55

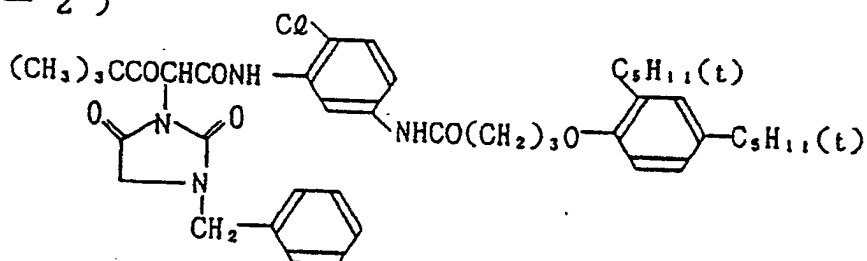
(H-2)



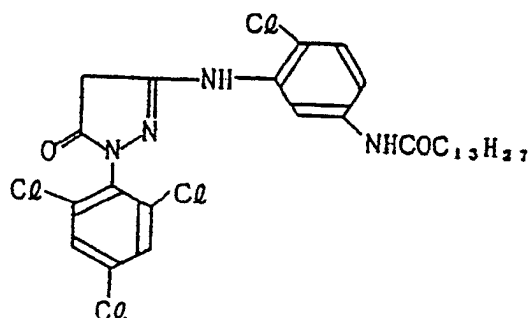
(H-3)



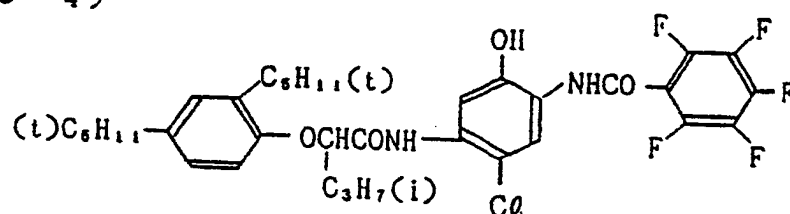
(Y-2)



(M-2)



(C-4)



The light-sensitive materials Samples 30 to 33 prepared in the above way were subjected to exposure to white light through an optical wedge, and then development processing according to the following steps to obtain neutral color positive images of the wedge.

The Dmax of the resulting cyan images was measured. Also measured was the retention of cyan images at the density 1.0 observed when the images were stored at 85°C under a relative humidity of 60% for 20 days. Results obtained are shown in Table 5.

	Processing steps:	(Processing temperature and processing time)	
[1]	Immersing in color developing solution	38 °C	8 sec
[2]	Fogging exposure	-	10 sec under 1 lux
[3]	Color developing	38 °C	2 min
[4]	Bleach-fixing	35 °C	60 sec
[5]	Stabilizing	25 to 30 °C	1 min 30 sec
[6]	Drying	75 to 80 °C	1 min

Composition of processing solutions:	
(Color developing solution)	
Benzyl alcohol	10 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g
Potassium bromide	1.5 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
3-Methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl) aniline sulfate)	5.5 g
Fluorescent whitening agent (a 4,4'-diaminostilbenedisulfonic acid derivative)	1.0 g
Potassium hydroxide	2.0 g
Made up to 1 l in total amount by the addition of water, and adjusted to pH 10.20.	

(Bleach-fixing solution)	
Ammonium ferric ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (a 70 % solution)	100 ml
Ammonium sulfite (a 40 % solution)	27.5 ml
Made up to 1 l in total amount by the addition of water, and adjusted to pH 7.1 using potassium carbonate or glacial acetic acid.	

(Stabilizing solution)	
5-Chloro-2-methyl-4-isothiazolin-3-on	1.0 g
Ethylene glycol	10 g
1-Hydroxyethylidene-1,1'-diphosphonic acid	2.5 g
Bismuth chloride	0.2 g
Magnesium chloride	0.1 g
Ammonium hydroxide (an aqueous 28 % solution)	2.0 g
Sodium nitrilotriacetate	1.0 g
Made up to 1 l in total amount by the addition of water, and adjusted to pH 7.0 using ammonium hydroxide or sulfuric acid.	

The stabilizing was carried out using a countercurrent system comprised of two tanks.

Table 5

Sample No.	Coupler	Dmax	Remaining rate
30 (X)	C-2	2.24	88 %
31 (Y)	C-4		
32 (")	Exemplary 10	2.41	94
33 (")	" 18	2.35	95
	" 35	2.30	95
X: Comparative Example			
Y: Present Invention			

As is shown above, the couplers of the present invention are seen to have a good thermal resistance.* The above light-sensitive materials were each loaded on Konicolor 7 (manufactured by Konica Corporation), and Color Checker (available from Macbeth Co.) was copied by scanning exposure at a constant rate of 5 cm/sec from a rectangular slit of 1 x 20 cm. As a result, Samples 31 to 33 showed distinct differences in the hue between cyan and blue, and more improved color reproducibility of green and red to magenta, than the comparative Sample 30.

Example 5

On a triacetyl cellulose film support having been applied with antistatic treatment at its back surface and subjected to subbing using a copolymer of maleic anhydride with vinyl acetate on the surface of the support to be coated with emulsion, the respective layers having the following composition were provided by coating from the support side to prepare a multi-layer color light-sensitive material Sample 34. The amount for addition is indicated as an amount per mol of silver halide unless particularly mentioned.

(Back surface antistatic treatment)

Back surface layer 1:

Stearic acid	20 mg/m ²
Diacetyl cellulose	10 mg/m ²
Alumina sol	1 g/m ²

Back surface layer 2:

Diacetyl cellulose	50 mg/m ²
Stearic acid	10 mg/m ²
Silica matting agent	50 mg/m ²
(average particle diameter: 3 μ m)	

(On the emulsion coating surface)

5

First layer: Anti-halation layer

10

Ultraviolet absorbent UV-2	0.3 g/m ²
Ultraviolet absorbent UV-3	0.4 g/m ²
Black colloidal silver	0.24 g/m ²
Gelatin	2.7 g/m ²

15

Second layer: Intermediate layer

20

2,5-Di-t-octylhydroquinone	0.1 g/m ²
Gelatin	1.0 g/m ²

25

Third layer: Low-speed red-sensitive silver halide emulsion layer

30

35

Monodisperse emulsion comprising AgBrI having an average grain size of 0.35 μ m and containing 12.5 mol % of AgI (Emulsion I)	0.5 g/m ² in silver weight
Sensitizing dye 1	7.6×10^{-4} mol
Coupler C-5	0.1 mol
Gelatin	0.9 g/m ²

1

40

Fourth layer: High-speed red-sensitive silver halide emulsion layer

45

Monodisperse emulsion comprising AgBrI having an average grain size of 0.75 μ m and containing 12.5

50

mol % of AgI (Emulsion II) 0.8 g/m² in silver weight

Sensitizing dye 1 3.2×10^{-4} mol

55

Coupler C-5 0.2 mol

Gelatin 1.75 g/m²

Fifth layer: Intermediate layer

5

2,5-Di-t-octylhydroquinone	0.1 g/m ²
Gelatin	0.9 g/m ²

10 Sixth layer: Low-speed green-sensitive silver halide emulsion layer

15

Emulsion I	1.0 g/m ² in silver weight
Sensitizing dye 2	6.6×10^{-4} mol
Sensitizing dye 3	0.6×10^{-4} mol
Coupler M-3	0.05 mol
Gelatin	0.8 g/m ²

20

Seventh layer: High-speed green-sensitive silver halide emulsion layer

25

Emulsion II	1.0 g/m ² in silver weight
Sensitizing dye 2	2.76×10^{-4} mol
Sensitizing dye 3	0.23×10^{-4} mol
Coupler M-3	0.15 mol
Gelatin	1.5 g/m ²

30

35 Eighth layer: Intermediate layer

The same as the fifth layer.

40 Ninth layer: Yellow filter layer

45

Yellow colloidal silver	0.1 g/m ²
Gelatin	0.9 g/m ²
2,5-Di-t-octylhydroquinone	0.1 g/m ²

50 Tenth layer: Low-speed blue-sensitive silver halide emulsion layer

55

5

Monodisperse emulsion comprising AgBrI having an average grain size of 0.6 μm and containing 12.5 mol % of AgI (Emulsion III)	0.4 g/m ² in silver weight
Spectrally sensitizing dye 4	2.65×10^{-4} mol
Coupler Y-3	0.3 mol
Gelatin	1.3 g/m ²

10

Eleventh layer: High-speed blue-sensitive silver halide emulsion layer

15

Monodisperse emulsion comprising AgBrI having an average grain size of 1.0 μm and containing 12.5 mol % of AgI (Emulsion IV)	0.8 g/m ² in silver weight
Spectrally sensitizing dye 4	1.59×10^{-4} mol
Coupler Y-3	0.3 mol
Gelatin	2.1 g/m ²

20

Twelfth layer: First protective layer

25

30

UV-2	0.3 g/m ²
UV-3	0.4 g/m ²
Gelatin	1.2 g/m ²
2,5-Di-t-octylhydroquinone	0.1 g/m ²

35

Thirteenth layer: Second protective layer

40

Non-light-sensitive fine grain silver halide emulsion comprising AgBrI having an average grain size of 0.06 μm and containing 1 mol % of AgI	0.3 g/m ² in silver weight
Polyethyl methacrylate particles (diameter: 1.5 μm)	
Gelatin	0.7 g/m ²
Surface active agent S-3	

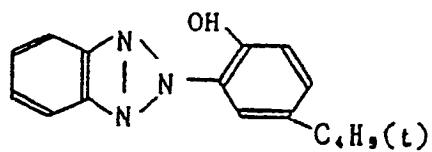
45

In each layer, H-1 and surface active agents were also added in addition to the above composition. Tricresyl phosphate was also used as a coupler solvent.

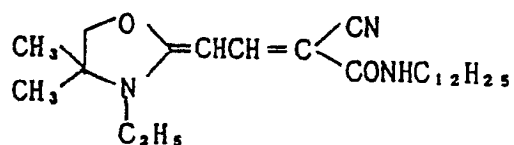
All the emulsions were monodisperse octahedral emulsions, obtained by making a seed emulsion of 0.095 μm or 0.25 μm (average silver iodide content: 2 mol %) grow according to a double-jet process in which the pAg and pH are controlled at 45°C in the presence of ammonia. The silver iodide contents in the core, intermediate layer and shell were controlled by changing the composition of the silver halide to be added.

In making the silver halide emulsion of a core/shell type grow, used were the methods as disclosed in Japanese Patent O.P.I. Publications No. 52238/1984, No. 138538/1985, No. 49938/1983 and No. 122935/1985. Compounds used in preparing the samples were as follows:

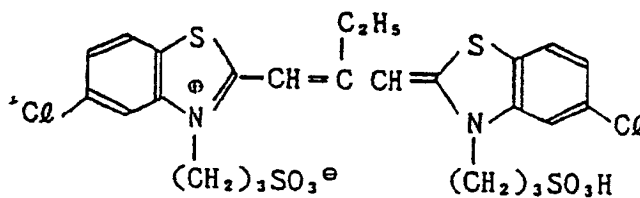
Ultraviolet absorbent UV-2



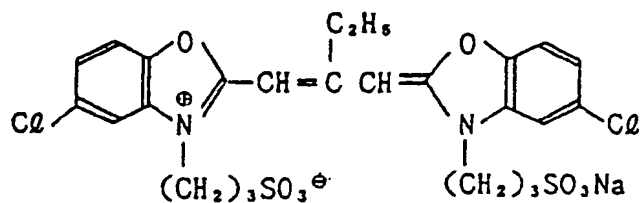
Ultraviolet absorbent UV-3



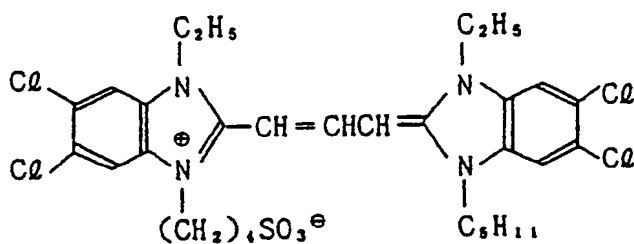
Sensitizing dye 1



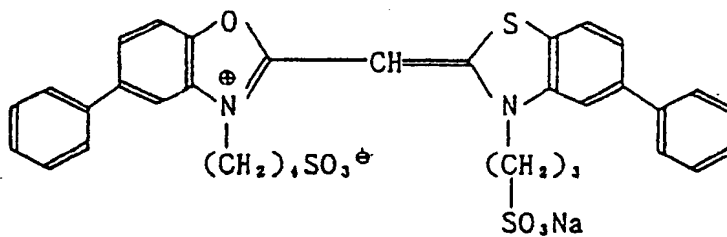
Sensitizing dye 2



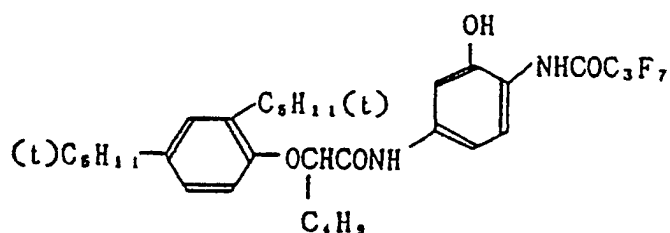
Sensitizing dye 3



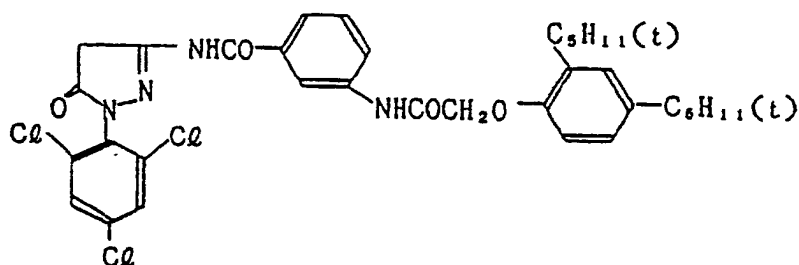
Sensitizing dye 4



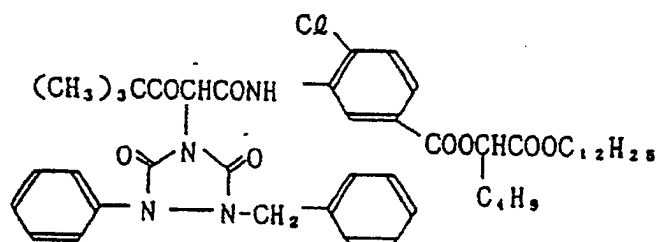
Coupler C-5



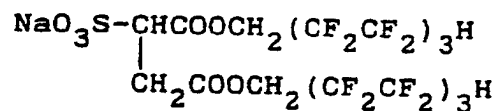
Coupler M-3



Coupler Y-3



Surface active agent 1



Light-sensitive materials were next prepared in which the cyan couplers used in the third layer and fourth layer of Sample 34 were replaced with Couplers 1, 4, 9 and 34 and the total weight of the third layer and fourth layer was reduced 30 %, which were designated as Samples 35, 36, 37 and 38, respectively. Samples 34 to 38 were subjected to the same processing as Sample 34.

Samples 34 to 38 were subjected to wedge exposure and the following reversal processing. Thereafter the Dmax of cyan images were measured under red light. Samples 34 to 38 were actually used to photograph a color checker (available from Macbeth Co.), followed by reversal processing. Thereafter the color reproducibility was visually compared.

Results obtained are shown in Table 6.

Processing steps	Processing time	Processing temperature
First developing	6 min	38 °C (± 0.3)
Washing	2 min	38 °C (± 0.3)
Reversing	2 min	38 °C (± 0.3)
Color developing	6 min	38 °C (± 0.3)
Compensating	2 min	38 °C (± 0.3)
Bleaching	6 min	38 °C (± 0.3)
Fixing	4 min	38 °C (± 0.3)
Washing	4 min	38 °C (± 0.3)
Stabilizing	1 min	Room temp.
Drying		

First developing solution	
Water	700 ml
Sodium tetrapolyphosphate	2 g
Sodium sulfite	20 g
Hydroquinone monosulfonate	30 g
Sodium carbonate (monohydrate)	30 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2 g
Potassium bromide	2.5 g
Potassium thiocyanate	1.2 g
Potassium iodide (a 0.1 % solution)	2 ml
Made up to 1,000 ml by the addition of water.	

Reversing solution	
Water	700 ml
Hexasodium nitrilotrimethylene phosphonate	3 g
Stannous chloride (dihydrate)	1 g
p-Aminophenol	0.1 g
Sodium hydroxide	8 g
Glacial acetic acid	15 ml
Made up to 1,000 ml by the addition of water.	

Color developing solution	
Sodium tetrapolyphosphate	2 g
Sodium sulfite	7 g
Sodium tertiary phosphate (dihydrate)	36 g
Potassium bromide	1 g
Potassium iodide (a 0.1 % solution)	90 ml
Sodium hydroxide	3 g
Citrazinic acid	1.5 g
N-methyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g
Ethylenediamine	3 g
Made up to 1,000 ml by the addition of water.	

Compensating solution	
Water	700 ml
Sodium sulfite	12 g
Sodium ethylenediaminetetraacetate (dihydrate)	8 g
Thioglycerol	0.4 ml
Glacial acetic acid	3 ml
Made up to 1,000 ml by the addition of water.	

Bleaching solution	
Sodium ethylenediaminetetraacetate (dihydrate)	2.0 g
Ammonium ferric ethylenediaminetetraacetate (dihydrate)	120.0 g
Ammonium bromide	100.0 g
Made up to 1,000 ml by the addition of water.	

Fixing solution	
Water	800 ml
Ammonium thiosulfate	80.0 g
Sodium sulfite	5.0 g
Sodium bisulfite	5.0 g
Made up to 1,000 ml by the addition of water.	

Stabilizing solution	
Water	800 ml
Formalin (37 wt.%)	5.0 ml
Konidax (a product of Konica Corporation)	5.0 ml
Made up to 1,000 ml by the addition of water.	

Table 6

Sample No.	Coupler	Dmax*
34 (X)	C-5	3.10
35 (Y)	Exemplary 1	3.26
36 (")	" 4	3.25
37 (")	" 9	3.23
38 (")	" 34	3.24

* Measured by red light

X: Comparative Example

Y: Present Invention

As will be seen from the above results, the samples of the present invention show Dmax more than the same as the comparative sample because of the higher molar absorptivity coefficient, even though the coating weights of the third layer and fourth layer are reduced.

As far as those on which Color Checker was actually photographed were visually evaluated, Samples 35 to 38 of the present invention also show a good distinction between cyan and blue, which is a feature of the coupler of the present invention, and show an improved color reproducibility of green and red.

Example 6

Silver halide emulsions prepared by the procedures as disclosed in Japanese Patent Application No. 31330/1983, which are core/shell silver iodobromide emulsions having a multi-shell structure such that the iodine content becomes lower from the iodine-rich inner shell in the inside of a grain toward the outer side layer, were chemically sensitized according to a conventional method. Coating solutions comprising the following additives were coated on a triacetyl cellulose film support successively from the support side to prepare a color light-sensitive material Sample 39 comprised of 13 layers.

First layer: Anti-halation layer

A gelatin layer containing black colloidal silver.

Gelatin: 1.2 g/m²

Second layer: Intermediate layer

A gelatin layer containing an emulsified dispersion of 2,5-di-t-octylhydroquinone.

Gelatin: 1.2 g/m²

Third layer: Low-speed red-sensitive silver halide emulsion layer

Monodisperse emulsion comprising octahedral silver iodobromide having an average grain size of 0.38 μ m and an average iodine content of 7.84 % (in weight ratio) (Emulsion I): 1.8 g/m² in silver coating weight

Sensitizing dye 5: 6×10^{-5} mol per mol of silver

Sensitizing dye 6: 1.0×10^{-5} mol per mol of silver

Sensitizing dye 7: 1.0×10^{-5} mol per mol of silver

Cyan coupler (C-6): 0.06 mol per mol of silver

Colored cyan coupler (CC-1): 0.003 mol per mol of silver

DIR Compound (D-1): 0.0015 mol per mol of silver

DIR Compound (D-2): 0.002 mol per mol of silver
Gelatin: 1.4 g/m²

5 Fourth layer: High-speed red-sensitive silver halide emulsion layer

Monodisperse emulsion comprising octahedral silver iodobromide having an average grain size of 0.65 μ m and an average iodine content of 7.37 % in weight ratio (Emulsion II): 1.3 g/m² in silver coating weight

Sensitizing dye 5: 3×10^{-5} mol per mol of silver

10 Sensitizing dye 6: 1.0×10^{-5} mol per mol of silver

Sensitizing dye 7: 1.0×10^{-5} mol per mol of silver

Cyan coupler (C-6): 0.02 mol per mol of silver

Colored cyan coupler (CC-1): 0.0015 mol per mol of silver

DIR Compound (D-2): 0.001 mol per mol of silver

15 Gelatin: 1.0 g/m²

Fifth layer: Intermediate layer

The same gelatin layer as the second layer.

20 Gelatin: 1.0 g/m²

Sixth layer: Low-speed green-sensitive silver halide emulsion layer

25 Emulsion I: 1.5 g/m² in silver coating weight

Sensitizing dye 8: 2.5×10^{-5} mol per mol of silver

Sensitizing dye 9: 1.2×10^{-5} mol per mol of silver

Sensitizing dye 10: 1.0×10^{-5} mol per mol of silver

Magenta coupler (M-4): 0.05 mol per mol of silver

30 Colored magenta coupler (CM-1): 0.009 mol per mol of silver

DIR Compound (D-1): 0.0010 mol per mol of silver

DIR Compound (D-3): 0.0030 mol per mol of silver

Gelatin: 2.0 g/m².

35 Seventh layer: High-speed green-sensitive silver halide emulsion layer

Emulsion II: 1.4 g/m² in silver coating weight Sensitizing dye 8: 1.5×10^{-5} mol per mol of silver

Sensitizing dye 9: 1.0×10^{-5} mol per mol of silver

Sensitizing dye 10: 7.0×10^{-6} mol per mol of silver

40 Magenta coupler (M-4): 0.020 mol per mol of silver

Colored magenta coupler (CM-1): 0.002 mol per mol of silver

DIR Compound (D-3): 0.0010 mol per mol of silver

Gelatin: 1.8 g/m²

45 Eighth layer: Intermediate layer

The same gelatin layer as the second layer.

Gelatin: 1.0 g/m²

50

Ninth layer: Yellow filter layer

A gelatin layer containing yellow colloidal silver and an emulsification dispersion of 2,5-di-t-octyl-hydroquinone.

55 Gelatin: 1.5 g/m²

Tenth layer: Low-speed blue-sensitive silver halide emulsion layer

Monodisperse emulsion (Emulsion I): 0.9 g/m² in silver coating weight
 Sensitizing dye 11: 1.3×10^{-5} mol per mol of silver
 Yellow coupler (Y-4): 0.29 mol per mol of silver
 Gelatin: 1.9 g/m²

5

Eleventh layer: High-speed blue-sensitive silver halide

emulsion layer

Monodisperse emulsion (Emulsion II): 0.5 g/m² in silver coating weight

10 Sensitizing dye 11: 1.0×10^{-5} mol per mol of silver

Yellow coupler (Y-4): 0.08 mol per mol of silver

DIR compound (D-2): 0.0015 mol per mol of silver

Gelatin: 1.6 g/m²

15 Twelfth layer: First protective layer

A gelatin layer containing;

silver iodobromide (AgI: 1 mol %; average grain size: 0.07 μ m); 0.5 g/m² in silver coating weight; and
 ultraviolet absorbers UV-2 and UV-3.

20 Gelatin: 1.2 g/m².

Thirteenth layer: Second protective layer (Pro-2)

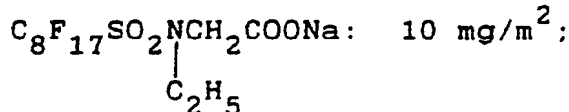
25 A gelatin layer containing;

polymethyl methacrylate particles (diameter: 1.5 μ m);

particles of an ethyl methacrylate/methyl methacrylate/methacrylic acid copolymer (average particle diameter: 2.5 μ m);

polydimethylsiloxane: 5 mg/m²;

30



35

and

a formalin scavenger (HS-1).

Gelatin: 1.2 g/m².

40 In each layer, a gelatin hardening agent (H-1) and a surface active agent were added in addition to the above composition.

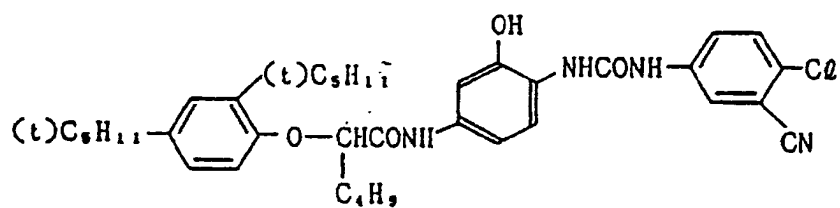
(Additives)

45

50

55

C - 6

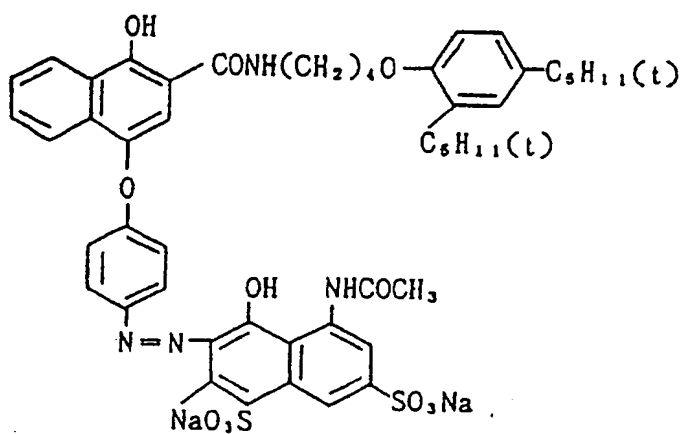


C C - 1

5

10

15

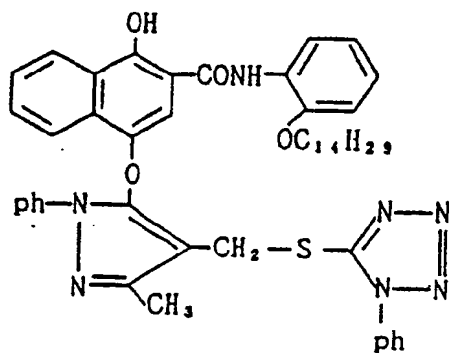


20

D - 1

25

30



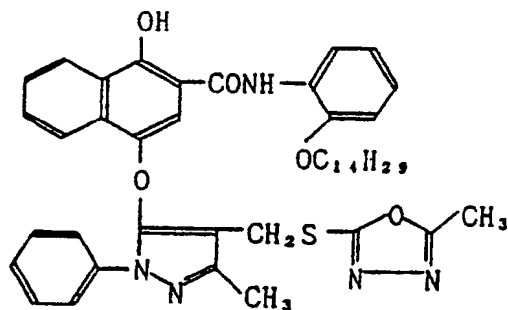
35

D - 2

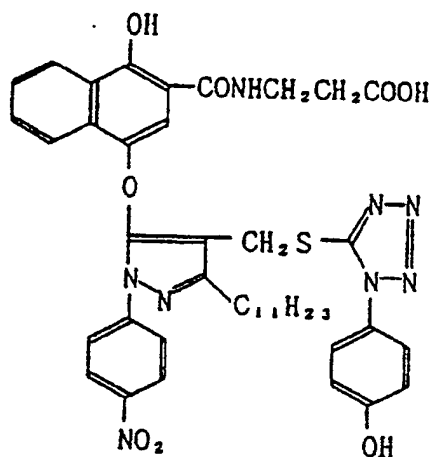
40

45

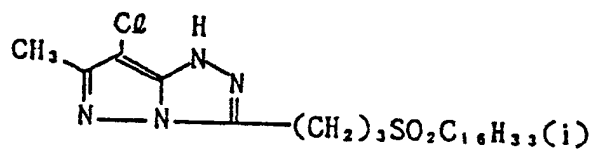
50



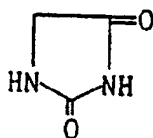
55



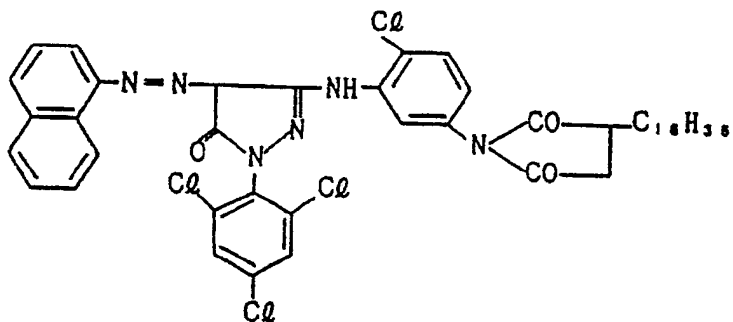
M - 4



H S - 1



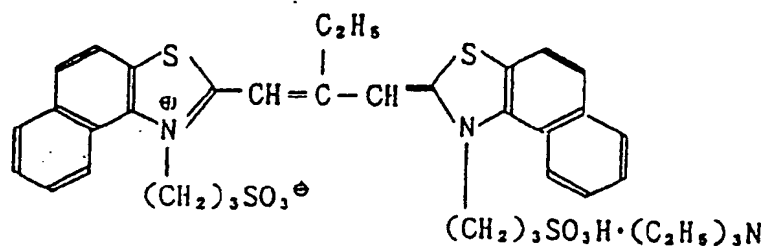
C M - 1



Sensitizing dye 5

5

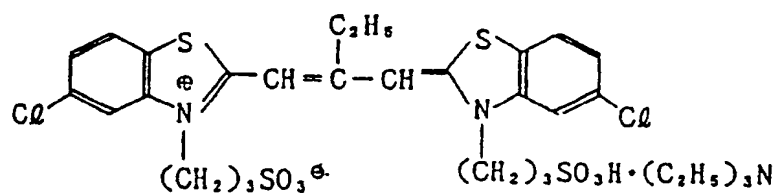
10



Sensitizing dye 6

15

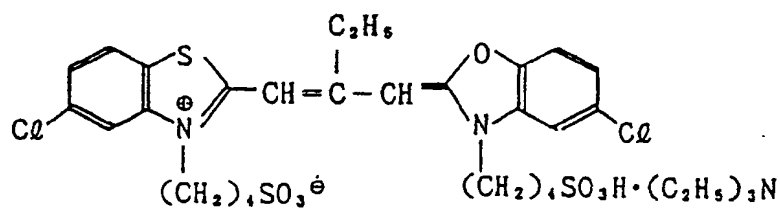
20



Sensitizing dye 7

25

30

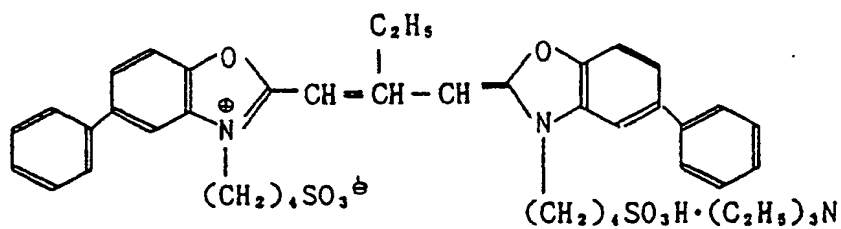


35

Sensitizing dye 8

40

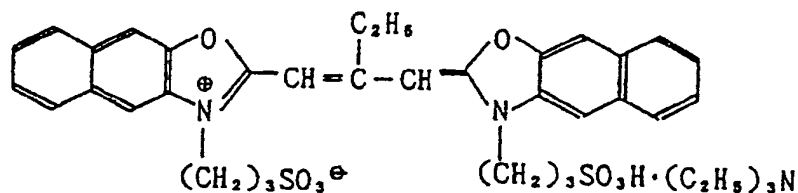
45



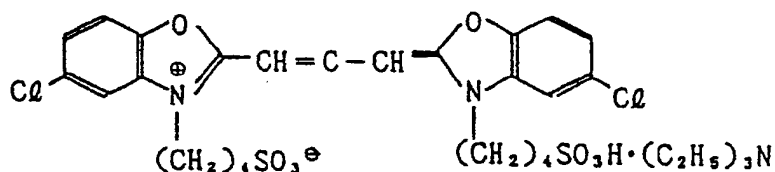
50

55

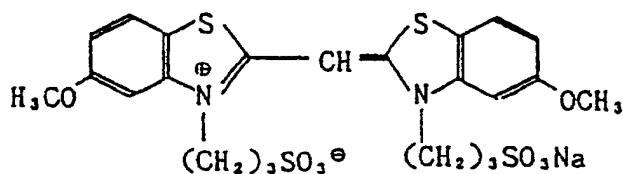
Sensitizing dye 9



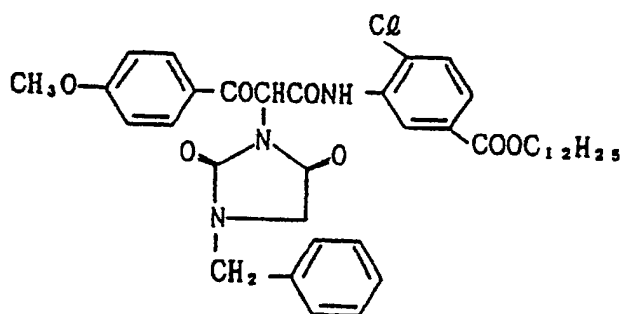
Sensitizing dye 10



Sensitizing dye 11



Y-4



Light-sensitive materials were obtained by replacing the cyan couplers used in the third layer and fourth layer, with the couplers 4, 6, 9 and 16 of the present invention as shown in Table 7, used in amount of 0.6 molar time the amount of the comparative coupler, and were designated as Samples 40, 41, 42 and 43.

The samples prepared in this way were subjected to wedge exposure using white light, the following development processing was carried out, and then the speed and fog of panchromatic layers were determined. The speed was indicated by a logarithm of the amount of exposure that gives a density of fog + 0.5, and shown as a relative value, assuming the speed of Sample 39 as 100.

Cyan images were also stored at 85 °C under a relative humidity of 60 % for 20 days, where the retention after deterioration, at the density 1.0 was measured. Results obtained are show together in Table 7.

Processing steps: (38 °C)	
Color developing	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec
Drying	

Processing solutions used in the respective processing steps had the following composition.

(Color developing solution)	
4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
Made up to 1 l by the addition of water.	

(Bleaching solution)	
Ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Made up to 1 l by the addition of water, and adjusted to pH 6.0 using ammonia water.	

(Fixing solution)	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3g
Made up to 1 l by the addition of water, and adjusted to pH 6.0 using acetic acid.	

(Stabilizing solution)	
Formalin (an aqueous 37 % solution)	1.5 ml
Konidax (a product of Konica Corporation)	7.5 ml
Made up to 1 l by the addition of water.	

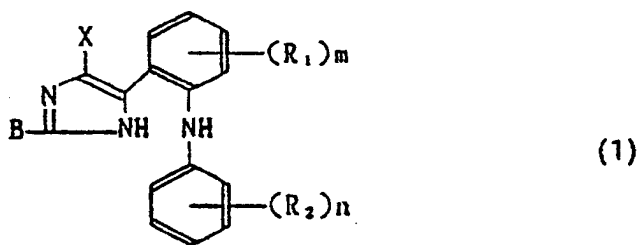
Table 7

Sample No.	Coupler	Speed	Remaining ratio
39 (X)	C-6	100	80 %
40 (Y)	Exemplary 4	118	91
41 (")	" 6	120	94
42 (")	" 9	120	93
43 (")	" 16	128	90
X: Comparative Example			
Y: Present Invention			

These results tell that the samples in which the couplers of the present invention are used can give a higher speed and have a superior thermal resistance irrespective of the smaller amount of couplers than that of the comparative sample.

Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon a silver halide emulsion layer containing a cyan coupler represented by the following formula I:



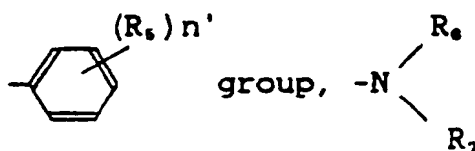
wherein B is an organic group comprising a carbon atom, nitrogen atom, oxygen atom or sulfur atom directly bonded to the imidazole ring; R_1 and R_2 each are a substituent; m is an integer of 0 to 4, n is an integer of 0 to 5, provided that the groups represented by said R_1 or R_2 are respectively allowed to be the same with or different from each other when m or n is 2 or more; and X is a group capable of being split off upon coupling reaction with the oxidation product of a color developing agent.

2. The material of claim 1, wherein said substituent represented by R_1 or R_2 is a halogen atom, a cyano group, a nitro group, a carboxy group, an alkyl group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an acyl group, an acyloxy group, an alkoxy-carbonyl group, an alkylamido group, an arylamido group, an alkylsulfonamido group, an arylsulfonamido group, a dialkylcarbamoylamino group, an alkoxy-carbonyl amino group, an aryloxy-carbonylamino group or a sulfamoylamino group.

3. The material of claim 1 or 2, wherein said organic group represented by B is an alkyl group, an aryl group, a heterocyclic group, a cyano group, a carboxyl group, an acyl group, a carbamoyl group, an alkoxy-carbonyl group, an aryloxy-carbonyl group, an acylamino group, alkoxy-carbonylamino group, aryloxy-

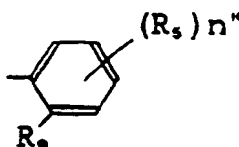
ycarbonylamino group, a sulfonamido group, an anilino group, a ureido group, a sulfamoylamino group, an amino group, an alkoxy group, an aryloxy group, a silyloxy group, a heterocyclic oxy group, an alkylthio group, an arylthio group or a heterocyclic thio group, these groups may have a substituent.

4. The material of claim 3, wherein said group represented by B is a



15 group of a $-LR_8$ group, wherein R_5 , R_6 , R_7 and R_8 are each a substituent; L is an oxygen atom or a sulfur atom, n' is an integer of from zero to 5, provided that the groups represented by said R_6 and R_7 are allowed to bond to form a ring and groups represented by R_5 may be the same with or different from each other when n' is 2 or more.

5. The material of claim 4, wherein said group represented by B is



25 wherein R_8 is a an amino group, an alkylamino group, an arylamino group, an alkylamido group, an arylamido group, an alkylsulfonamido group, an arylsulfonamido group, dialkylcarbamoylamino group, alkoxycarbonylamino group, an aryloxycarbonylamino group or a sulfamoylamino group; and n'' is an integer of zero to 4.

30 6. The material of claims 1 or 2 to 5, wherein said cyan coupler is contained in said silver halide emulsion layer in an amount of from 10 g to 300 g per mol of silver halide contained in said emulsion layer.

THIS PAGE BLANK (USPTO)

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



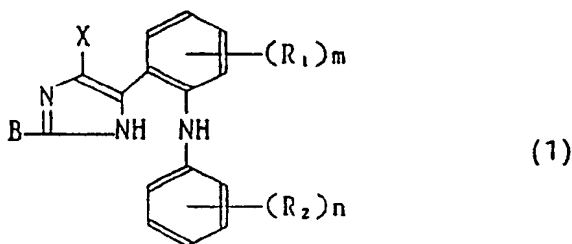
(11) Publication number:

0 354 549 A3

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **89114720.9**(51) Int. Cl.⁵: **G03C 7/38, //C07D233/54**(22) Date of filing: **09.08.89**(30) Priority: **12.08.88 JP 202270/88**(43) Date of publication of application:
14.02.90 Bulletin 90/07(84) Designated Contracting States:
DE GB(98) Date of deferred publication of the search report:
10.04.91 Bulletin 91/15(71) Applicant: **KONICA CORPORATION**
26-2, Nishishinjuku 1-chome, Shinjuku-ku
Tokyo 160(JP)(72) Inventor: **Masukawa, Toyooki**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Uchida, Takashi**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Nakayama, Noritaka**
Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)(74) Representative: **Türk, Gille, Hrabal**
Brucknerstrasse 20
W-4000 Düsseldorf 13(DE)(54) **Silver halide photographic lightsensitive material containing novel cyan coupler.**

(57) A silver halide color photographic light-sensitive material is disclosed, which has a silver halide emulsion layer containing a novel cyan coupler represented by the following Formula I:



wherein B is an organic group comprising a carbon atom, nitrogen atom, oxygen atom or sulfur atom directly bonded to the imidazole ring; R₁ and R₂ each are a substituent; m is an integer of 0 to 4, n is an integer of 0 to 5, provided that the R₁s or R₂s each may be the same with or different from each other when m or n is 2 or more.; and X is a group capable of being split off upon coupling reaction with the oxidation product of a color developing agent.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 11 4720

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
P,X	EP-A-0320778 (KONICA) * page 5, lines 33 - 43 * * page 33, lines 15 - 16 * ---	1-6	G03C7/38// C07D233/54
X,D	EP-A-0249453 (KONISHTROKU) * page 2, line 63 - page 3, line 61 * * page 13, lines 7 - 9 * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 FEBRUARY 1991	Examiner MAGRIZOS S.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone V : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (03.82) (P0401)